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Higher Alcohols in the Alcoholic Distillation From Fermented Cane Molasses.

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HIGHER ALCOHOLS IN THE ALCOHOLIC DISTILLATION FROM FERMENTED CANE MOLASSES

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ABSTRACT

Fusel oil is the name given collectively to a mixture of alcohols higher in molecular weight than ethanol, obtained as by-products in the alcoholic fermentation industries. Iso-amyl, active-amyl, iso-butyl and n-propyl alcohols are generally the main constituents of fusel oil with n-amyl, n-butyl and iso-propyl alcohols generally present in lesser amounts. In addition, minute amounts of a wide variety of organic substances appear as impurities in the fusel oil by-product.

The main constituent alcohols of fusel oil are derived from amino acids present in the mash and formed by autolytic breakdown of the proteins of the cells themselves. The origin of n-butyl and iso-propyl alcohols is traced to the action of butyric acid bacteria on sugar.

The composition of fusel oil and the amount produced in any particular fermentation depends on the kind of substrate utilized, nitrogen source present, nature of the microorganism employed, time and temperature of fermentation process, and contaminations present in the mash.

Fusel oil is used commercially as a solvent, frother agent, anti-foaming agent, and as process material in the chemicals industry. Amyl acetate is the most important derivative of fusel oil.

A review was made on the various methods of analysis available for the determination of fusel oil. The A.O.A.C. procedure, based on the Allen-Marquardt method, reports only about 60% of the true fusel oil present. Colorimetric methods, based on Komarowsky's reaction, possesses greater accuracy and sensitivity and are less time consuming.

The presence of fusel oil over certain limits in alcoholic beverages and industrial alcohol detracts from the quality of the product. In continuous distillation process the oils are separated as a side-stream from an intermediate region of the rectifying column.

In this work experimental data have been gathered on fusel oil distribution in the rectifying column under different operating conditions. The data can be used for design purposes and for the selection of operating conditions in commercial practice in order to produce distillates of definite specifications.

The experimental results obtained indicate that: (1) the location of the plate of maximum accumulation is a function of the reflux ratio utilized and the alcohol content in the feed; (2) under the operating conditions studied, a single peak of fusel oil accumulation occurs and it is always above the feed plate in the region where the apparent alcohol content is from about 130° to 140° Proof; (3) the width of the fusel oil band is a function of the operating conditions utilized; (4) different concentrations of fusel oil occur in plates of similar alcohol content under different operating conditions; (5) variations in the content of fusel oil in the feed do not cause a shift in the location of the plate of maximum concentration; (6) reflux ratios of 2:1 or below do not product predominant accumulations in any region of the column; distillates very high in fusel oil are produced; (7) there is no fusel oil present in the alcohol-exhausted plates in the bottom of the column.

An automatic control system was developed for the operation of continuous distillation columns in the alcoholic distillation, based on

varying the rate of feed to maintain constant a reference temperature in the column.

Graphs were prepared, based on experimental data, for determining true alcohol content in samples containing large concentrations of fusel oil.

Liquid-vapor equilibrium data for the system ethanol-water at one atmosphere was compiled in a single tabulation which gives the equilibrium compositions for both phases in terms of per cent by weight, mol fraction and per cent by volume at 60°F and 20°C. Direct conversions between the various terms can be readily made.

CHAPTER I

ORIGIN AND COMPOSITION OF FUSEL OIL

Whenever pure yeast is allowed to ferment in a sugar containing substrate with the presence of a suitable nitrogenous diet and the proper mineral salts, the liquor at the end of the fermentation contains not only alcohol but also minute amounts of a considerable number of other substances arising from the metabolism of the cell.

Prominent among the great variety of substances found in solution are inorganic salts and acids, alcohols, aldehydes, ketones, glycerol, esters, organic acids, essential oils and gases such as carbon dioxide. In addition, the mash contains solid impurities consisting in greater part of nitrogen compounds such as yeast cells, albuminoids and pectic substances. Glycogen, yeast gum, complex organic phosphates, as well as other substances are also present (2, 143).

The nitrogenous compounds are easily decomposed when submitted to heat in the distillation process, producing volatile substances which, if not removed during the distillation, are responsible for undesirable odor and flavor characteristics in the final product. In contaminated mashes, hydrogen and gaseous compounds of sulphur are frequently found due to powerful bacterial reducing action on sulphates and sulphites present in the mash. The impurities listed above exist in very small quantities and in some cases mere traces.

The alcohols present as impurities in fermented liquors are of special interest to the chemical engineer responsible for the design and operation of distilling plants.

Due to their particular behavior in the distillation of fermented mashes, their elimination from the process presents some technical difficulties. This group of impurities consists of a number of aliphatic alcohols higher in molecular weight than ethyl alcohol. Isoamyl and active amyl (d-amyl) alcohols are usually the chief constituents present, followed by n-propyl and isobutyl alcohols. In addition, isopropyl, n-butyl and n-amyl alcohols are present in smaller amounts. Only primary alcohols are believed to be present. These alcohols accumulate and are removed together as a by-product during the course of the distillation process. This by-product usually contains a small per cent of other impurities such as high boiling esters, fatty acids, aldehydes and other substances. The higher alcohols take-off is designated collectively with the name of "fusel oil". The term is applied loosely to designate the higher alcohols by-product in various degrees of purification. In the plant it is applied to the stream withdrawn from continuous distillation columns or to a given fraction from intermittent distillation processes, both of which are relatively rich in higher alcohols, but containing large amounts of ethyl alcohol and water. The concentrated product resulting after submitting the raw take-off to cooling, extraction with water and decantation is designated as decanted or crude fusel oil. Further, fusel oil also designates a highly purified mixture of higher alcohols obtained by dewatering and fractional distillation of the above mentioned less pure mixtures. The latter is called "refined fusel oil" in order to differentiate it in the marketing of the by-product.

Concentrated fusel oil is a yellow or brownish, volatile, oily

liquid with a disagreeable, nauseating taste and characteristic suffocating odor. The refined product is a colorless liquid retaining most of the taste and odor characteristics of the crude product. The term "fusel oil" is derived from the German "Fusel", meaning bad spirits.

Fusel oil was discovered in 1785 by the Swedish pharmacist Scheele and the physician Westendorf (124, 143). The latter found that it could be separated from raw alcoholic distillates by subsequent distillation, but a good number of years elapsed from this discovery until a practical solution to the problem was obtained in the alcohol industry. It was not until 1862 that a reactifying apparatus from which fusel oil was obtained simultaneously as a by-product, was installed at the Stengel alcohol factory in Leipzig (144).

Constituents of Fusel Oil

In 1834, Dumas studied two samples of fusel oil separated from commercial ethyl alcohol by distillation (24). The samples were fractionated by Dumas and the fractions boiling from 130° to 132°C analyzed for their constituent elements. The results obtained were as follows:

	Sample I %	Sample II %	Calculated for Amyl Alcohol, %
Carbon	69.3	68.6	68.2
Hydrogen	13.6	13.6	13.6
Oxygen	17.1	17.8	18.0

The calculated values for amyl alcohol are included for comparison (124).

It was Cahours in 1839 who discovered that the essential constituent of fusel oil produced from the fermentation of potatoes, which was the same

as that isolated by Dumas by fractional distillation, contained the radical C_5H_{10}- and that it was nothing else than the hydrate of amylene or amyl alcohol (10). This fact was later confirmed by Dumas and Stas (25).

Biot discovered that the alcohol isolated by Dumas and later by Cahours was optically active, but it is Pasteur who proved that it consists of a mixture of two amyl alcohol isomers (104, 105). The studies of Pasteur indicate that both alcohols are similar in their chemical properties, differ but slightly in density and boiling point, and yield, under similar circumstances, two products which resemble each other in all properties except in optical activity, the active alcohol always giving active products while the inactive always results in inactive products. Pasteur found the active alcohol to boil at 127-128°C while the inactive boiled at 129°C under ordinary atmospheric pressure. Presently accepted values are 128°C for the active d-amyl, and 132°C for the inactive isoamyl (107).

The structural formulas of these two alcohols are:

d-amyl -- $CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot OH$

isoamyl - $CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot OH$

Pasteur found that the proportion of the alcohols in fusel oil vary depending on its origin. That from fermentation of molasses contains about equal parts of the two alcohols while that from the fermentation of grains contains about 1/3 of the active and 2/3 of the inactive alcohol.

The attention of numerous workers of the time was drawn toward studies designed to ascertain the composition of fusel oil.

Wartz discovered, in 1852, the presence of isobutyl alcohol in commercial fusel oil (155).

In 1853, Chancel discovered a new alcohol in fusel oil which he identified as n-propyl alcohol (14).

The work of other investigators confirmed the presence of n-propyl, isobutyl, active amyl and isoamyl alcohols in fusel oil (19, 98, 152). For some time these four alcohols accompanied with smaller amounts of high boiling esters, acids, aldehydes and other substances were considered the main constituents of fusel oil.

In papers published in 1778 and 1880, Rabuteau reported the presence of isopropyl, n-butyl and n-amyl alcohols in commercial fusel oils (114, 118). These reports were originally overlooked. Other authors reported analyses of fusel oils in which these alcohols had been found amoung other constituents (18, 49, 51, 103). It was Pringheim, however, who called attention toward the overlooked work of Rabuteau and offered new experimental findings which confirmed these results (114, 116). More recent data has confirmed the presence of these alcohols in some fusel oils (26, 59, 81, 119, 150).

Numerous workers have studied the nature of the group of substances normally present in commercial fusel oil and which constitute the higher boiling fractions and residue obtained upon fractional distillation of the oil.

Aliphatic alcohols of molecular weight higher than amyl have been identified in fusel oils from different origins (8, 26, 60, 102, 103, 120, 136, 150). They consist of isomers of the hexylic, heptylic, octylic, nonylic and decylic series. Swenarton has indicated that in the fraction boiling higher than decyl alcohol there are small quantities of alcoholic

material of still higher molecular weights (136).

The acid constituents have been studied extensively and the isolation and identification of a large number of them have been reported in the literature. Formic, acetic, propionic, butyric, valeric, caproic, enanthic, caprilic, pelargonic, capric, lauric, myristic, palmitic, and other fatty acids of more than 16 carbon atoms have been found (8, 12, 13, 52, 58, 61, 69, 71, 80, 89, 120, 130, 148). In addition, the presence in very small amounts of linoleic and various mono-ethylenic acids have been reported (112).

Esters form another important constituent of the higher boiling fractions of commercial fusel oil. Their presence has been reported on numerous occasions (8, 26, 27, 52, 58, 60, 69, 71, 103, 117, 148, 150).

In addition to alcohols, acids and esters, the presence of a rather large number of substances have been reported in the literature. Among them, the following are listed: aldehydes (60, 117, 148), furfural (26, 52, 58, 71, 148), lower ketones (52), pyridine and other bases (8, 16, 26, 120, 125), terpenes (102, 120), SO_2 and amines (148), hydrocarbons (26, 131) and others (103, 130, 137, 157).

Origin of Fusel Oil

Several theories were offered to explain the formation of higher alcohols during the course of the fermentation. The origin of these alcohols was usually sought in the sugar present in the mash to be fermented, from which they were believed to be formed by the yeast itself or by bacteria present while others traced their formation to the direct reduction of fatty acids (5, 50, 108, 110, 111, 112, 113, 116).

It was Ehrlich, however, who conclusively showed in his classical researches that the main higher alcohols, and probably also the aldehydes, contained in fusel oil are in reality derived from the amino-acids which are formed by the hydrolysis of proteins present in the mash and to a lesser extent from the protein of the cells itself.

The close relationship between the formula of leucine, which is:

$$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH(NH_2) \cdot COOH$$

and isoamyl alcohol,

$$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot OH$$

had previously suggested that some relation might exist between these two substances, but there was no experimental confirmation of the idea.

In 1903, Ehrlich discovered that proteins also yield on hydrolysis as isomeride of leucine, known as isoleucine, which has the constitution

$$CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH$$

and has to d-amyl alcohol

$$CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot OH$$

the same relation as leucine to isoamyl alcohol (29, 30, 39, 37, 38, 41, 47, 48).

This fact attracted his attention to the problem of the origin of amyl alcohols in alcoholic fermentation.

Ehrlich utilized pure yeast cultures, thus eliminating the participation of bacteria, to ferment sterilized sugar solutions to which amino acids had been added. He found that leucine readily yielded isoamyl alcohol and isoleucine gave d-amyl alcohol (31, 32, 36, 37, 38, 40). The following are typical results of the experiments conducted (65):

(I) In an experiment carried out without the addition of leucine the

amount of fusel oil produced was 0.4% based on pure ethyl alcohol. (II) When 6 grams of synthetic optically inactive leucine were added, 2.11% of fusel oil were produced which were also inactive. 2.5 grams of leucine were recovered, thus, the fusel oil produced was equivalent to 87% of the theoretical yield of isoamyl alcohol. (III) In the presence of 2.5 grams of isoleucine, 1.44% of fusel oil was produced corresponding to 80% of the theoretical yield of d-amyl alcohol from the isoleucine added (65).

This change, which Ehrlich has termed the alcoholic fermentation of amino acids, requires the presence of living cells. Ehrlich and Pringsheim showed that when either zymin or yeast juice is substituted for the intact organism the change does not occur (9, 35, 112). Ehrlich also showed experimentally that the change is not effected even by living cells in the absence of fermentable sugars (37, 38).

Other a-amino acids undergo this same type of reaction. Ehrlich showed that isobutyl alcohols are derived from valine, i.e., a-amino-isovaleric acid (31, 143).

The origin of n-propyl alcohol is attributed to a-amino-n-butyric acid while that of n-amyl alcohol is traced to norleucine, i.e., a-amino-n-caproic acid (59). The formation of isopropyl and n-butyl alcohol, on the other hand, does not provein from the deamination of amino acids, but its origin is traced to the action on sugar of butyric acid bacteria present in the mash (51, 114, 116). This probably explains the rather low concentrations of these alcohols generally found and its absence in numerous cases. The composition of fusel oils from different sources will be discussed in later paragraphs.

The chemical reactions involved in the deamination of the amino acids listed above are represented by the following equations:

(1) $CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O = CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot OH + CO_2 + NH_3$

Leucine — isoamyl alcohol

(2) $CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH + H_2O = CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot OH + CO_2 + NH_3$

Isoleucine — d-amyl alcohol

(3) $CH_3 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH + H_2O = CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot OH + CO_2 + NH_3$

Valine — Isobutyl alcohol

(4) $CH_3 \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O = CH_3 \cdot CH_2 \cdot CH_2 \cdot OH + CO_2 + NH_3$

a-amino-n-butyric acid — n-propyl alcohol

(5) $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O = CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH + CO_2 + NH_3$

norleucine — n-amyl alcohol

Other a-amino acids undergo similar changes and the reaction appears to be a general one. Ehrlich and Pistschimucka utilized tyrosine, i.e., $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$ to produce tyrosol, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot OH$ which was first prepared in this manner (43, 46). This substance has a very bitter taste and is probably related to the flavor of beer. In a similar manner phenylalanine is converted into phenylethyl alcohol while tryptophan yields tryptophol which was first prepared in this way by Ehrlich (45).

The reaction is closely related with the nitrogenous metabolism of the cell and the ammonia formed by this process is immediately utilized by the yeast for building up albuminous matter. No free ammonia is detected in the mash in the course of the fermentation (37, 38).

In the course of his studies, Ehrlich proved with experimental

data that if a more readily assimilable nitrogen source is present, such as contained in ammonium salts and aspargine, the yeast takes its supply of nitrogen mainly from them without splitting up the amino acids to the same extent and consequently less fusel oil is formed (37, 38). These results were confirmed by Pringsheim (112, 113, 116), and later by Kurono (83). Ehrlich found that the addition of ammonium carbonate to a mash lowered the production of fusel oil from 0.70% to 0.33% based on pure ethyl alcohol. The addition of leucine alone raised the yields of fusel oil from 0.70% to 2.78%. However, the addition of both, leucine and ammonium carbonate resulted in the formation of only 0.78% of fusel oil. The production of fusel oil, therefore, as well as the nature of its constituents, depends on the composition of the medium to be fermented.

Ehrlich also found in his studies that the yield of fusel oil is affected by the condition of the yeast in regard to nitrogen. In solutions of sugar and leucine, yeasts poor in nitrogen produce comparatively more fusel oil, due to the more ready decomposition of amino acids than is the case when yeasts well supplied with nitrogenous materials are utilized. The nature of the carbonaceous nutriment and the nature of the yeast utilized proved to be of great importance (47, 48).

Another finding which resulted from Ehrlich's experiments is the fact that even in pure sugar solutions and in total absence of amino acids, the yeast always produces some fusel oil during the course of the fermentation. Its own albumin is partly split-up ' autolysis into amino acids such as leucine, isoleucine and valine, which are, in turn, transformed into fusel oil. The nitrogen thus produced is utilized again for the

construction of the protein of the cell (37, 38, 65). Houssiau has pointed out along these same lines that, as cells die and new ones are formed, the resulting nitrogenous compounds may appear in subsequent metabolism indistinguishable from those derived from aspargine, amino acids, amides, proteins, etc., present in molasses or other medium, and are even used again in the formation of cells. This accounts for the lack of proportionality in the yield of fusel oil and the nitrogen content of the molasses or slops (70).

Numerous workers have confirmed the findings of Ehrlich in the course of the years.

Yomada, in Japan, and Genovois, in France, have studied the effect of adding various ammonium salts and other nitrogen nutriments to reduce the formation of fusel oil (62, 157). Unpublished results obtained at the Rum Pilot Plant of the Agricultural Experimental Station of the University of Puerto Rico, utilizing Puerto Rican molasses have indicated that 2/3 lb. of ammonium sulphate, fertilizer grade, per 100 gallons of mash at approximately 24°Bx., would yield minimum contents of fusel oil in the fermented mash. Addition of larger amounts would not produce any siginificant reduction in the production of fusel oil. The use of smaller amounts, on the other hand, not only increases the yields of fusel oil, but also increases the length of time required for completion of the fermentation process.

Arroyo found, in Puerto Rico, working with cane molasses, that the amount of fusel oil produced is smaller if a special yeast strain is selected, the fermentation is performed at 25-27°C and the nitrogen required by the yeast is supplied in the form of ammonium hydroxide (4).

Zalesskaya and Konolev confirmed that the formation of fusel oil depends on the content of nitrogenous substances in the substrate and on the ability of the yeasts to utilize amino acids. Removal of supplementary nitrogen during the course of fermentation of molasses contributes to the deamination of leucine with the corresponding increase in fusel oil (164).

Dietrich and Klammerth confirmed that in the absence of sugar no fusel oil was formed from leucine (22).

Other workers have studied other factors regarding the formation of fusel oil during fermentation. Segal studied the inhibiting effects of the higher alcohols in the fermentation process and found that the injurious effects are greater the higher the alcohol in the homologues series. Fusel oil sharply retards fermentation at 0.4% and inhibits it completely at 0.7% to 0.8% referred to the mash (127). Shichiji and co-workers found that fusel oil added to the mash in quantities over 0.1%, referred to the solution, inhibited fermentation and reproduction of yeast (128).

There are several reports in the literature on studies conducted regarding the stage of the fermentation process at which formation of fusel oil begins (11, 60, 63, 79, 82, 162). There are discrepancies among the published results. The formation of fusel oil in one case was found to precede that of ethyl alcohol while in other cases the reverse was found to be true (79). In other cases it is reported that the formation of fusel oil coincides with the formation of ethanol (11, 82, 162).

In recent researches, Castor and Guyman obtained data on the

relationship between the course of fusel oil formation, multiplication of yeast cells, utilization of amino acids naturally present in the mash and the conversion of sugar to ethanol in the alcoholic fermentation of grape juice (11).

The results obtained showed that the course of fusel oil formation was concurrent with that of ethanol production, rather than with amino acid disappearance or yeast cell multiplication. The greater part of the total amount of fusel oil was formed after both rapid cell multiplication and rapid loss of amino acids had ceased. The amounts of the amino acids present diminished rapidly to low levels within 18 to 37 hours after starting the fermentation and thereafter there were only slight changes in their concentration, in general, a slow, steady increase. Yeast cell multiplication ceased between 45 and 50 hours after the fermentation was started, whereas formation of ethanol and fusel oil continued up to about 170 hours.

At the 37th hour, when the rapid decrease of amino acids has ceased, only about 34% of the theoretical yield of fusel oil had been obtained. However, at the end of the fermentation, the amount of higher alcohols found greatly exceeded the theoretical yield expected. At the 168th hour, the actual yield amounted to 255% of the theoretical.

The authors pointed out that the failure of approximately equivalent amounts of higher alcohols to appear concurrently with the disappearance of their amino acid precursors might, at first sight, suggest that the Ehrlich scheme--which postulates that by the deamination of amino acids ammoniacal nitrogen is furnished for the synthesis of protein during

yeast cell multiplication--was directly involved only to a limited extent during the yeast cell multiplication stage of the fermentation process. The idea of direct assimilation by yeast of intact amino acids, earlier advanced by Thorne on the basis of evidence not concerned with fusel oil formation, could explain the findings (138). The latter production of large amounts of fusel oil could, in turn, be explained by the idea postulated by Ehrlich and Harden that yeast can form fusel oil by the autolytic breakdown of its own protein which yields the amino acid precursors of fusel oil (37, 65). The measurable increase in the concentration of amino acids during the stage of alcoholic fermentation subsequent to the cessation of rapid yeast multiplication, suggests that during that stage of the fermentation process, amino acids were being produced at a somewhat faster rate than that at which they were converted into higher alcohols.

On the basis of the Neubauer-Fromherz mechanism--which postulates that the most likely early intermediates in the formation of fusel oil are ketnoic acids, later decarboxylated to aldehydes and subsequently reduced to alcohols--and on the findings that,(1) there is a time lag between the assimilation of amino acids and the appearance of fusel oil, (2) the formation of ethanol and fusel oil occur concurrently, and (3) the cessations of both processes occur simultaneously, the authors offer a simple explanation for the relationship between the conversion of sugar to ethanol and the formation of fusel oil. They suggest that it is likely that the final steps of both of these metabolic processes make use of one or more identical enzyme systems. The slow appearance of the higher

alcohols could be explained by competition between large amounts of sugar fermentation intermediates and small amounts of fusel oil intermediates, for the carboxylase and the hydrogen-transferring alcohol dehydrogenase-Coenzyme I systems of the zymase complex. When the supply of sugar fermentation intermediates, which yield hydrogen to Coenzyme I, failed because of the disappearance of sugar, the hydrogen transfer system could no longer reduce the aldehyde precursors of fusel oil components, thus the formation of both ethanol and higher alcohols would simultaneously be terminated. The yield of fusel oil in excess of theoretical expectations would be explained by ideas discussed in preceding paragraphs that yeast can form fusel oil at the expense of its own protein.

The experimental results of Castor and Guyman confirm previous observations by workers on the subject. In 1938, Zalesskaya observed that the most energetic formation of fusel oil coincides with the beginning of the main fermentation of sugar when the multiplication of yeast and the deamination of amino acids is nearly concluded (162). With a strong yeast innoculum, which results in shorter fermentation time, the formation of fusel oil was found to stop simultaneously with the production of ethanol at the end of 36 hours. The splitting of amino acids by yeast took place rapidly, up to 70% of them being consumed in 12 hours. With conditions which produced longer fermentation times the yield of fusel oil was greater. Its formation took place slowly and continued uniformly until the main fermentation was concluded. Autolytic breakdown of yeast cell protein in larger amounts explains the greater yields of fusel oil during longer fermentation times.

In 1949, while studying the capacity of yeasts to utilize nitrogen from various amino acids, Konovalov observed that the formation of fusel oil begins only after the first stage of the fermentation process (82).

The influence of time of fermentation on the production of fusel oil in the alcoholic fermentation has been the subject of several studies. In all cases, it has been found that the amount of fusel oil produced increases with longer fermentation time (11, 60, 63, 128, 162). Glimm, studying the fermentation of beer, and Shichiji, working with cane molasses, found that the formation of fusel oil varies with time reaching a limit which remains unchanged thereafter (63, 128).

The discoveries of Ehrlich, that the yield of fusel oil could be increased up to 7%, based on ethyl alcohol, with the addition of suitable proportions of amino acids, sugar and yeast innoculum, gave rise, in the early years of the century, to several patents and proposed processes for the production of large amounts of fusel oil. At that time the commercial utilization of fusel oil in several applications, especially for the production of solvents and the suggestion of its use as raw material for isoprene and butadiene, needed in the synthetic rubber industry, greatly increased the demand and the price of fusel oil (143). Ehrlich obtained patents in Germany, England and in this Country for a process based on his discoveries (32, 36, 40). Darco Sales Corporation obtained a British patent for a process based on promoting the fermentation of fusel oil (and other fermentations) by adding to the fermenting mash an active absorbent agent as activated vegetable charcoal together with organic nitrogenous food substances (21). Sultan and Stein patented a process

in France, in 1907, based on adding leucine to the fermenting mash (134, 135).

Fernbach and Strange obtained a British patent on a process based on producing higher alcohols by treating yeast, such as that remaining from alcoholic fermentation processes, in the presence or absence of carbohydrates with a proteolytic ferment such as tyrothrix tenuis, and a ferment such as the butylic bacillus of Fitz (57).

Several authors have reviewed the methods of commercial production of fusel oil (90, 95, 139, 141, 161).

Reaction Mechanism for the Deamination of Amino Acids

There have been several mechanisms proposed through which group--$CH(NH_2)$--could be converted into the terminal group--$CH_2 \cdot OH$--appearing in the alcohol.

(1) One way in which the change may possibly be effected is by the direct elimination of carbon dioxide with subsequent hydrolysis of the resulting amine as follows (65):

(a) $R \cdot CH(NH_2) \cdot COOH = R \cdot CH_2(NH_2) + CO_2$

(b) $R \cdot CH_2(NH_2) + H_2O = R \cdot CH_2 \cdot OH + NH_3$

Reaction (a) has been found to be actually effected by some bacteria but there is no direct evidence that it can be effected by yeast (66).

Ehrlich and Pistschimuka have found that many wild yeasts actually bring about the change represented by equation (b) in which the amine is hydrolized to the corresponding alcohol (46). With ordinary yeast cultures only traces of amylamine are converted into amyl alcohol while yeasts which form surface growth, such as willia anomala, produce the change

readily in the presence of sugar, glycerol or ethyl alcohol as sources of carbon.

(2) Ehrlich originally suggested as a possible mechanism the formation of an a-hydroxy-acid which was subsequently decomposed into an alcohol and carbon dioxide or into an aldehyde and formic acid, the aldehyde being reduced to the alcohol and the formic acid destroyed (34):

(a) $R \cdot CH(NH_2) \cdot COOH + H_2O = R \cdot CH(OH) \cdot COOH + NH_3$

(b) $R \cdot CH(OH) \cdot COOH = R \cdot CH_2 \cdot OH + CO_2$ or

(c) $R \cdot CH(OH) \cdot COOH = R \cdot CHO + HCOOH$ and

(d) $R \cdot CHO + H_2 = R \cdot CH_2 \cdot OH$

(3) Neubauer and Fromhertz proposed a scheme which consists of the oxidative removal of the $-NH_2$ group with the formation of an a-ketonic acid (100). The a-ketonic acid is subsequently decomposed into carbon dioxide and an aldehyde, the latter being either reduced to an alcohol or oxidized to an acid:

(a) $R \cdot CH(NH_2) \cdot COOH + 1/2\ O_2 = R \cdot CO \cdot COOH + NH_3$

(b) $R \cdot CO \cdot COOH = CO_2 + R \cdot CHO$

(c) $R \cdot CHO + H_2 = R \cdot CH_2OH$ or

(d) $R \cdot CHO + 1/2\ O_2 = R \cdot COOH$

The researches of Neubauer established that amino acids actually yield the corresponding a-ketonic acid when treated with yeast in a sugar solution (100). He further demonstrated that, under similar conditions, the a-ketonic acid produces good yields of the alcohol containing one less

carbon atom while the corresponding a-hydroxy-acid, contrary to Ehrlich's suggestion, yields only extremely small amounts of the alcohol. The researches of Neuberg have shown that all races of brewers and wine yeasts readily convert a-ketonic acids into an aldehyde and carbon dioxide, as depicted by equation (b), by the enzyme carboxylase (101). Further, the ready conversion of the aldehyde into alcohols and acids by yeast has been proved. This would explain the many times recognized presence of the valeric acid and aldehyde (143).

Based on the above mentioned facts, Harden concludes that this mechanism for the alcoholic fermentation of amino acids is the most probable course (65).

Composition of Fusel Oil from Different Substrates

It has been mentioned in previous paragraphs that the composition of the fusel oil produced in a given fermentation will depend on a number of factors such as the nature of the mash, nitrogenous substances present, type and condition of the yeast with regard to nitrogen, time of fermentation and others.

Table 1 gives the composition of various fusel oils from different origins reported in the literature. The composition figures are based on the alcohol-water-free oil. The reference number of the source of information is given.

It can be observed from the data tabulated that there are rather wide variations in the composition of the fusel obtained even when the same kind of substrate was utilized in the fermentation. This is a confirmation that the nature of the carbohydrate source used is not the only factor affecting the composition of the oil produced. It may also be

TABLE 1

COMPOSITION OF FUSEL OIL FROM DIFFERENT ORIGINS ON ALCOHOL-WATER-FREE BASIS

	Substrate	Active Amyl	Iso-Amyl	n-Amyl	Iso-Butyl	n-Butyl	Iso-Propyl	n-Propyl	Hexyl + Higher	Acids, Ald., Esters, etc.	Undetermined	Ref. No.
1	Cane Molasses	-----	55.3	-----	4.3	7.4	8.1	0.6	24.3	---	---	---	59,81
2	Cane Molasses	-----	85.0	-----	---	---	---	2.0	---	---	2.8	8.2	27
3	Cane Molasses	-----	55.4	-----	4.1	7.4	8.1	0.7	24.3	---	trace	---	119
4	Cane Molasses	-----	95.4	-----	---	0.2	0.4	2.5	0.3	0.6	3.8	---	132
5	Cane Molasses	-----	65.3	-----	---	1.9	5.6	18.9	3.4	0.4	1.7	2.8	132
6	Cane Molasses	-----	69.8	-----	---	0.2	0.4	19.4	0.5	0.4	3.1	6.2	132
7	Beet Molasses	-----	59.8	-----	---	14.4	7.2	---	15.1	0.3	0.3	2.9	132
8	Beet Molasses	41.4		26.3	8.1	6.1	6.1	4.0	---	Trace	3.0	5.0	8
9	Grapes	-----	24.5	-----	---	---	63.8	---	11.7	---	---	---	18,103
10	Grapes	-----	34.4	-----	---	4.5	49.3	---	11.9	---	---	---	18
11	Grapes	9.6		54.0	trace	18.3	6.8	---	4.1	1.5	5.6	0.1	150
12	Grapes	-----	63.2	-----	---	7.7	8.9	---	15.7	0.4	0.2	3.9	132
13	Grapes	-----	85.2	-----	---	2.8	---	---	12.0	---	---	---	143
14	Potato	-----	34.4	-----	---	30.4	4.4	18.8	3.8	---	0.8	7.4	132
15	Potato	-----	68.8	-----	---	24.4	---	---	6.8	---	---	---	58,59,81
16	Potato	-----	31.5	-----	6.9	5.7	7.4	17.2	3.4	---	8.6	19.3	117
17	Potato	-----	68.7	-----	---	24.4	---	---	6.9	---	trace	---	143,152
18	Potato	28.6		24.0	0.5	4.2	---	6.5	5.2	0.1	---	30.9	102
19	Corn	14.6		36.3	---	23.9	---	---	20.4	---	---	4.8	59,81
20	Corn	23.4		59.7	---	12.2	---	---	11.7	---	---	3.0	59,81
21	Corn	-----	87.4	-----	---	9.8	---	---	2.7	---	---	---	1
22	Corn	-----	64.3	-----	---	17.6	8.4	---	4.0	1.3	0.3	4.1	132
23	Barley	-----	47.7	-----	---	5.6	5.9	---	35.7	0.9	0.3	3.9	132
24	Rye	-----	79.8	-----	---	15.7	---	---	---	---	---	6.5	59,81
25	Wood Sugar	-----	68.8	-----	---	15.9	---	---	2.2	---	---	13.1	53
26	Wood Sugar	-----	74.4	-----	---	20.5	---	trace	0.3	---	1.0	3.8	52
27	Sulfite Waste	9.9		49.3	---	16.9	2.0	---	2.0	2.8	10.4	6.7	69
28	Unknown	-----	67.4	-----	---	21.8	---	---	10.8	---	---	---	88
29	Unknown	-----	68.0	-----	---	24.0	---	---	7.0	---	trace	1.0	94

observed that in several cases the analysis was performed on only a fraction of the original oil containing the main constituents, while in other cases the complete mixture was analyzed.

Yields of Fusel Oil from Different Raw Materials

According to the information available in the literature, the yields of fusel oil obtained in commercial practice may vary between 1 and 11 gallons per 1000 gallons of absolute alcohol produced, depending upon the substrate used, nitrogenous substances added, conditions of the fermentation and the distillation process used. Table 2 gives average figures reported in the literature.

TABLE 2

YIELDS OF FUSEL OIL FROM DIFFERENT RAW MATERIALS

Source	Fusel Oil, Gal. per 1000 gal. of alcohol	Reference No.
Blackstrap molasses	2.6	67
Blackstrap molasses	4 - 5	59, 81
High-test molasses	1 - 3	59
Evaporated cane juice	1 - 2	59
Corn	4 - 5	59, 81
Degerminated corn	2.5 - 3	59, 81
Wheat	2 - 3	59, 81
Rye	2 - 4	59, 81
Grains (mixed)	5.3	67
Sulphite liquor	2 - 3	59
Potatoes	5 -11	59

Fusel Oil Content in Alcoholic Beverages

Fusel oil is normally present in varying amounts in all kinds of alcoholic beverages. Its proportion depends on the nature of the beverage.

Much has been written regarding the toxic effects supposedly produced by the fusel oil present in beverages, to the extent that the belief was long held that the injurious effects of beverages such as whiskey, brandy and rum were due mainly, if not wholly, to their fusel oil content. As a result of recent researches on the subject, it is now accepted that the toxic effects of fusel oil, in the proportion that it exists in beverages, have been greatly exaggerated and that it is probable that the predominating agent in the whiskey which produces physiological effects is the ethyl alcohol (153).

Table 3 presents data on fusel oil content of several commercial beverages that have been reported in the literature. The values given below for strong spiritous beverages, such as rum, brandy and whiskey, have been converted, when necessary, to a basis of 100 milliliters of product at 86°P.

TABLE 3

FUSEL OIL CONTENT IN ALCOHOLIC BEVERAGES

Kind of Product	Fusel Oil, mgs. per 100 ml. of product	Reference No.
1. Beer	1.7 - 3	132
2. Sherry Wine	3 - 5	132
3. Madeira Wine	5 - 7	132
4. Port Wine	8 - 10	132
5. Claret Wine	3 - 5	132
6. White Wine	2 - 4	132
7. Red Wine	4 - 6	137
8. California White Table Wine	16 - 37	64
9. California Red Table Wine	14 - 42	64
10. California Dessert Wine	16 - 90	64
11. Cider	3 - 5	132
12. Gin	5 - 40	132
13. Gin	19	153
14. Cognac Grandy, 10 years old	54	153
15. Henessy Brandy, 2 years old	253	132
16. Martel Brandy, 10 years old	354	132
17. Jamaica Rum	95 - 108	132
18. Puerto Rican Rum	32 - 60	3, 77
19. Demerara Rum	50	153
20. Rum, unknown origin	39	132
21. Dewar Whiskey, 5 years old	189 - 224	132
22. House of Lords Whiskey	217 - 265	132
23. Scotch Whiskey	69 - 86	154
24. Irish Whiskey	88	154
25. Bourbon Whiskey, unknown origin	668	132
26. American Rye Whiskey	73 - 167	154
27. American Rye Whiskey	78 - 132	20
28. American Bourbon Whiskey	89 - 130	154
29. American Bourbon Whiskey	101 - 124	20
30. Country Spirits	923 -1254	132

CHAPTER II

COMMERCIAL USES OF FUSEL OIL

For many years fusel oil was an almost valueless by-product of the alcohol industry. It was utilized as illuminating oil and in other minor applications. It was later used as a solvent in the explosive and paint industries but its use was abandoned in favor of cheaper solvents (176). During the early years of the century, however, fusel oil became a very valuable substance. It was largely used as a source of amyl alcohol for the production of amyl acetate which in turn was used in large quantities as a solvent for nitrocellulose in the making of varnishes, lacquers, and artificial leathers having a nitrocellulose composition. The use of fusel oil was extended to other industries. In the fruit essence industry, it was separated into its constituent alcohols by fractional distillation. These, in turn, were subsequently converted into their corresponding esters of several acids and used for flavoring liquors, jellies, sweets and the like. Fusel oil and its constituent alcohols were employed for the precipitation of asphalt from heavy mineral oils (176).

As a result of the methods worked out by Perkins, Mathews and others for converting isoamyl alcohol into isoprene and n-butyl alcohol into butadiene, the use of fusel oil as raw material for synthetic rubber was suggested (179).

In 1900-1901, the oil was sold in Germany at 50 M. for 100 kilos, or 4-1/2 lbs. a shilling. By 1910, its price had risen to 170 M. per 100 kilos and, in 1912, it was quoted in England at 140 pounds of sterling per

ton. The world supply, in 1912, was estimated at 3,500 to 6,000 tons a year. With the advent of Fernbach's patent, discussed in Chapter I, it was stated that it could be produced in unlimited amounts at 35-40 pounds sterling per ton (176, 186).

The United States, in 1910, imported 495,000 lbs. with a value of $598,000. No less than 50,000 gallons of amyl acetate were annually consumed in the United States at that time for solvent purposes (176, 186).

Because the limited supply of fusel oil was insufficient to meet the increasing demands for high boiling solvents for use in automotive lacquers, the production of synthetic amyl alcohols commenced in 1926 (173). The process consists of chlorinating in the vapor phase a mixture of pentanes from natural gas gasoline. In a distillation unit the amyl chloride isomers are separated from any polychloropentanes as well as from unreacted pentanes and hydrogen chloride. The amyl chlorides are subsequently hydrolized to the corresponding alcohols (167, 169, 170, 174). The final product contains all possible amyl alcohol isomers with the exception of 2,2-dimethyl-1-propanol. Specifications for synthetic amyl alcohol are available in the literature (166, 173).

Specifications for Fusel Oil and Amyl Alcohol

Fusel oil is supplied commercially in a crude and refined grade. The specifications vary from case to case. The following typical specifications are given in the literature:

1. Crude Fusel Oil (173):

Color	yellow
Odor	strong

Boiling Range:
- up to 122°C - 34%
- 122-138°C - 61%
- above 138°C - 3.4%

d_{20}^{20} - 0.83

Solubility in saturated NaCl - - - - - - - - - - - - - - - - - - 3%

Ethyl Alcohol, % by volume - - - - - - - - - - - - - - - - - - 1.7

2. Refined Fusel Oil (173, 183):

Color - Water-white

Odor - Nonresidual

Boiling Range:
- Below 110°C - None
- Below 120°C - Less than 15%
- Below 130°C - Above 60%
- Above 135°C - None

d_{20}^{20} - 0.811 - 0.815

Acidity as acetic acid, maximum - - - - - - - - - - - - - - - 0.02%

Dryness, miscibility with 20 volumes of 60°Be.
- gasoline at 20°C - No turbidity

Nonvolatile matter, maximum - - - - - - - - - - - - - - - - - 0.005%

3. Refined Fusel Oil (177):

Coefficient of expansion per 1°F - - - - - - - - - - - - - - 0.00051
per 1°C - - - - - - - - - - - - - - 0.00092

Color - Water-white

Dryness, miscibility with 20 volumes of 60°Be gasoline
- at 20°C - No turbidity

Evaporation Rate at 95°F (in minutes): 5% - - - - - - - 3-1/2
25% - - - - - - -17
50% - - - - - - -36-1/2
75% - - - - - - -64-3/4
90% - - - - - - -90-1/4
95% - - - - - - 103-1/2

Flash Point - 108°F (Approx.)

Residue on evaporation - None

d_{20}^{20} - 0.811 - 0.815

Weight per gallon at 20°C - - - - - - - - - - - - - - - - - 6.76 lbs.

Acidity as acetic acid, maximum - - - - - - - - - - - - - - - 0.01%

Boiling Range:
- Below 100°C - None
- Below 110°C - Not over 10%
- Below 120°C - Not over 30%
- Below 130°C - Not less than 90%
- Above 145°C - None

Nonvolatile matter, maximum - - - - - - - - - - - - - - 0.005%

4. Refined Amyl Alcohol (183):

Color - Water-white
Odor - Nonresidual
Distillation Range:
Below 126°C - None
Above 132°C - None
d_{20}^{20} - 0.811 - 0.815
Acidity as acetic acid, maximum - - - - - - - - - - - - 0.02%
Dryness, miscibility with 20 volumes of 60°Be.
gasoline at 20°C - - - - - - - - - - - - - - - - - No turbidity
Nonvolatile matter, maximum - - - - - - - - - - - - - - 0.003%

Production and Imports of Fusel Oil and Amyl Alcohol

Data regarding the production of fusel oil is meager. The information presented in Table 4, published by the United States Tariff Commission, includes both fusel oil and amyl alcohol. Quantities produced and imported, as well as the corresponding value in dollars for selected years between 1929 and 1947 are given (185).

TABLE 4

PRODUCTION AND IMPORTS OF AMYL ALCOHOL AND FUSEL OIL

Year	Production		Imports	
	Quantity, lbs.	Value	Quantity, lbs.	Value
1929	---	---	52,467	$ 10,737.00
1935	11,002,667	$ 1,430,347.00	3,292	1,948.00
1937	14,205,997	1,988,840.00	2,605	699.00
1938	9,096,977	1,091,637.00	179	69.00
1939	---	---	754	308.00
1943	14,250,000	1,996,000.00	---	---
1946	15,475,000	2,321,000.00	136,941	13,228.00
1947	17,728,000	3,191,000.00	32,511	1,949.00

The data presented indicates the increasing trend in the production of fusel oil and amyl alcohols. It can be observed that the value of the imports is insignificant averaging less than 1.0% of production. Fusel oil generally accounts for a predominant part of the imports.

Mellan gives the data presented in Table 5 in the allocations of amyl alcohols, including all grades and sources, for the period between April 1--June 30, 1945 (177):

TABLE 5

ALLOCATIONS OF AMYL ALCOHOLS FROM APRIL 1--JUNE 30, 1935

Use	Amount, lbs.	Per Cent
Total allocations	4,630,000	100.0
Amyl acetate, all grades	2,345,000	50.7
Lacquers and solvents	1,279,000	27.7
Ore flotation reagents	418,000	9.0
Drugs and Pharmaceuticals	235,000	5.1
Adhesives	180,000	3.9
Petroleum refining	44,000	1.0
Miscellaneous uses	122,000	2.6

Of the amyl acetate produced, 20% was used in the production of penicillin, 73% in lacquers and 7% in other applications.

Uses of Amyl Alcohols and Fusel Oil

The industries in which fusel oil and the amyl alcohols find application are listed in the literature with varying degree of completeness (172, 173, 176, 177, 178, 182). One of the most complete accounts is probably that given by Gregory from which most of the information presented

below is taken (172). In all cases the information available consists of generalities lacking specific information regarding amounts used, potential market and specific stage of the process in which utilized.

In the chemical industry fusel oil and the alcohols obtained from it find use as general solvents for alkaloids, camphor, fats, iodine, phosphorous, resins, sulphur and others. They serve as solvents miscible with ethyl alcohol, ether and essential oils. They also serve as process material in organic synthesis and act as starting point in making amyl acetate, amyl butyrate, amyl formate, amyl oleate, amyl oxalate, amyl phthalate, amyl propionate, amyl tartrate, and pharmaceutical chemicals such as amyl nitrate, amyl valerate, amyl formate and amyl barbital.

In the perfume industry, refined fusel oil and amyl alcohols are used for the production of amyl benzoate and amyl salicylate.

In the manufacture of cellulose products, they find use as ingredients of solvent mixtures for cellulose acetate, nitro cellulose and cellulose esters and ethers.

Amyl alcohols find use in the mining industry as frothers for the flotation of nonferrous ores. Aleinikov has found that mixing them with ethyl xanthate gives better results and affords considerable savings of the oil and ethyl xanthate in the flotation of quartzitic copper sulfide ores (165).

The amyl alcohols and fusel oil are used as antifoaming agents and are intermediate in the manufacture of photographic chemicals.

Due to their solvent power they are used as diluents for hydraulic fluids of the castor oil type, in rifle bore cleaners, gum inhibitors,

printing inks and in lacquers (173).

Fusel oil and amyl alcohols are used as solvents in numerous other industries including the beverage industry for the production of flavoring syrups and extracts; coating compositions in the ceramic industries; solvent for aromatic agents and cellulosic bases in cosmetics; compositions containing nitrocellulose and resins used for insulating and coating in the electrical industries; gelatinizing agent and solvent for nitrocellulose in the manufacture of explosives; solvent for fats, essential oil and waxes; solvent in making fruit flavoring syrups and extracts; solvent in compositions containing nitrocellulose and resins in the plastics, rubber, textile, paints, paper, glass, leather and metal fabricating industries. It is also used as gloss imparter and promotor of good flowing properties in dopes, lacquers, enamels, paints and varnishes.

CHAPTER III

ANALYTICAL METHODS FOR THE DETERMINATION OF FUSEL OIL

The most widely used methods of analysis for the determination of fusel oil can be grouped into two general classifications. The first group comprises the volumetric methods which depend upon the extraction of the higher alcohols with an organic solvent. The second group includes the colorimetric methods which are based on measuring the intensity of the color produced by reactions exhibited by the higher alcohols but not by ethyl alcohol.

The better known volumetric methods are the Rose-Herzfeld method, largely used in Germany, and the Allen-Marquardt method, generally employed in England and which forms the base of the official method of the Association of Official Agricultural Chemists in this Country.

Among the colorimetric methods that of Mohler-Rocques constitutes the official French method while that based on Komarowsky's reaction has been used in American and through Europe. It constitutes the official method in Switzerland (222). The introduction of rather recent modifications to Komarowsky's method has resulted in greater precision and ease of application with the corresponding increase in the acceptance of the method by the alcohol industry (202, 216, 240).

Several reviews of the various methods are available in the literature (168, 205, 216, 222, 239, 240).

Volumetric Methods

Rose-Herzfeld Method: This method is based on the greatest solubility of the higher alcohols in chloroform than in ethyl alcohol itself. Accordingly, the sample to be tested is shaken with a measured volume of chloroform and the higher alcohols are estimated from the increase in volume of the chloroform. In the original method described by Rose, the sample was adjusted to 50% alcohol by volume corresponding to a specific gravity of 0.96564 at 15.5°C referred to water at 15.5°C (245). One hundred milliliters of the sample so adjusted were shaken with 20 milliliters of chloroform in a graduated vessel at 15.0°C. With the aid of a table and the height of the layer of chloroform the quantity of fusel oil is determined. In order to eliminate from the sample substances interferring with the method, Stutzer and Reitmair introduced a procedure for treating the sample before the analysis (254). The treatment consisted of boiling the sample at total reflux with small amounts of sodium or potassium hydroxide with subsequent distillation of the resulting liquor and completing the distillate to the original volume.

Herzfeld and Windish modified Rose's apparatus for conducting the extraction providing graduations of 0.01 centimeter (222). The alcohol concentration in the sample was modified to 30% by volume.

The analytical procedure, with the above mentioned modifications, is given as follows by Kervegant (222):

To eliminate the interferring impurities, treat 100 milliliters with several drops of concentrated potassium hydroxide; boil under total reflux for one hour and then distill the largest part of the liquid and

complete the volume of the distillate to the original 100 milliliters. Adjust the alcohol content of the sample to 30% by volume and cool to 15°C. Add pure chloroform at about 15°C into a modified Rose tube up to the 20 ml. mark maintaining the tube into a water bath at 15°C. Give about 5 minutes for both tube and chloroform to come to thermal equilibrium and make sure that exactly 20 ml. of chloroform have been added. At this moment add into the tube 100 milliliters of the sample adjusted to 30% alcohol by volume and at 15°C. Maintain the tube inside the water bath at 15°C at all times. Add one milliliter of sulfuric acid diluted to a density of 1.286 and mix thoroughly the contents of the tube. The purpose of the acid is to help later in the separation of the chloroform. Agitate inside the water bath at 15°C for 15-20 minutes making sure that intimate contact is obtained between the two liquid phases. Leave the tube in the bath for one hour at the end of which the reading is taken. Simultaneously with the above operation, pure alcohol diluted to 30% by volume at 15°C is treated with chloroform in identical fashion. The difference between the increase in volume in the two tubes will determine the concentration of higher alcohols present in the sample. For that purpose, previously prepared tables are used.

In order to obtain reliable results by the Rose-Herzfeld method great care is required in the manipulation. Under those circumstances it usually gives results of the correct order of magnitude (240). The alcoholic strength should be carefully adjusted since variations of 0.1% would produce a difference of 0.0199% in the volume of the higher alcohols (222). A difference of 1.0°C produces a variation of 0.1 milliliters in

the chloroform layer while a concentration of one part of amyl alcohol in one thousand parts of sample at 30% alcohol and 15°C corresponds to an increase of 0.2 milliliters. The purity of the chloroform and the calibration of the apparatus used are also factors of great importance. The increase in the volume of chloroform produced by a given concentration of fusel oil depends on the higher alcohols present in any particular case. The relative coefficients of expansion at 30% ethyl alcohol and 15°C are as follows (222):

Amyl alcohols	1.00
n-Butyl alcohol	0.57
Isobutyl alcohol	0.50
n-Propyl alcohol	0.33
Isopropyl alcohol	0.13

The method has the disadvantage of comparing the increase in volume of chloroform to that produced by pure ethyl alcohol and not to that of a fusel oil standard containing the various higher alcohols in a proportion similar to the sample.

The presence of impurities in the fusel oil sample would affect the results. The pretreatment of the liquor to be tested does not remove all impurities possibly present. In addition, the method is time consuming, the adjustment of the original sample to exactly 30% at 15°C being very tedious.

Allen-Marquardt Method: This method is based on the extraction of the higher alcohols by carbon tetrachloride in which they are more readily soluble than in ethyl alcohol, washing the carbon tetrachloride free from traces of ethyl alcohol, oxidation of the extracted alcohols to the corresponding acids, distillation and titration of the acids formed (263).

In the original method described by Marquardt, 150 milliliters of the brandy to be analyzed are diluted with an equal volume of water and extracted three times with carbon tetrachloride utilizing 50 milliliters of the latter in each extraction (189, 236). The combined carbon tetrachloride extracts are thoroughly washed with water to remove any ethyl alcohol and then heated in a closed flask for six hours at 85°C with 5 grams of potassium bichromate, 30 grams of water and 2 grams of sulfuric acid. After the completion of the oxidation, the mixture is distilled, water added to the residue and the distillation continued. The distillate is boiled for half an hour with barium carbonate under total reflux. The carbon tetrachloride is then distilled off, the residue filtered and the filtrate evaporated to dryness. The residue is weighed and then dissolved in water containing a few drops of nitric acid. From this solution, the amount of barium salts of fatty acids was determined and the amount of fusel oil present in the original sample calculated.

The Allen-Marquardt method has been extensively modified in the course of the years and at present the procedure which constitutes the official method of the Association of Agricultural Chemists is as follows (190, 263):

To 50 milliliters of the sample, in a 500 milliliter Erlenmeyer flask, add 50 milliliters of water and 20 milliliters of 0.5N, sodium hydroxide, and connect the flask with a condenser, using standard taper ground glass connections, and distill off 90 milliliters, slowly at first, then more vigorously toward the end; add 25 milliliters of water and continue the distillation until an additional 25 milliliters are collected.

If aldehydes are present in excess of 15 parts in 100,000, add to the distillate 0.5 grams of metaphenylenediamine hydrochloride, boil under reflux condenser an hour, distill 100 milliliters, add 25 milliliters of water, and continue the distillation until an additional 25 milliliters are collected. Approximately saturate the distillate with finely ground sodium chloride and add saturated sodium chloride solution until the specific gravity is 1.10. Extract this sodium chloride solution four times with purified carbon tetrachloride, using 40, 30, 20 and 10 milliliters, respectively, and wash the combined carbon tetrachloride extracts 3 times with 50 milliliter portions of saturated sodium chloride solutions, and twice with saturated sodium sulphate solution. Then transfer the carbon tetrachloride layer to a flask containing 50 milliliters of an oxidizing solution prepared by dissolving 100 grams of potassium bichromate in 900 milliliters of water and adding 100 milliliters of sulfuric acid; boil for 8 hours under a reflux condenser. Add 100 milliliters of water and distill until only about 50 milliliters remain. Add 50 ml. of water and again distill until 35-50 milliliters are left. Use extreme care to prevent the oxidizing mixture from burning and baking on the sides of the distilling flask. Distillate should be water white; if it is colored, discard it and repeat determination. Titrate distillate with 0.1N sodium hydroxide, using phenolphthalein indicator. 1.0 milliliters of 0.1N sodium hydroxide are equivalent to 0.0088 grams of amyl alcohol. Make a blank determination on the carbon tetrachloride, beginning at the point in the procedure immediately after extraction and just before the carbon tetrachloride is washed with the sodium chloride solution.

This method has long been known to be subject to errors but the magnitude of these errors has not been generally realized (240). Dudley made a comparative study of the Allen-Marquardt and the Rose-Herzfeld methods and found that the results given by the latter method were from 2.0 to 2.5 times those obtained by the former. He concluded, however, that the Rose method was greatly in error. The results of Penniman and co-workers, among others, have shown the reverse to be true (240).

Penniman found that the A.O.A.C. method reports an average of about 60% of the total fusel oil actually present, although under certain conditions the accuracy may be as low as 40%. The results indicate that the errors in this method vary with the composition and concentration of fusel oil (240). The A.O.A.C. method is affected by variations in technique and by uncontrolled factors such as the temperature at which the extractions are conducted. In a given case in which amyl alcohol was the only alcohol used, the reports of eleven laboratories on the same sample varied from 42% to 145% of the total amyl alcohol actually present (240). In their studies, Penniman and co-workers also determined that the errors in the method partly occur in the oxidation stage and partly in the extraction and washing stages. More recent investigations by other workers have totally confirmed the results of Penniman (216, 232, 262).

In addition to the limitations listed, the method is laborious and time consuming.

Colorimetric Methods

Mohler-Rocques Official French Method: The earliest form of colorimetric method for the determination of higher alcohols in ethanol liquors,

consisted of treating the sample to be examined with sulfuric acid which produced colored products. This reaction, indicated by Dumas, was used by Savalle for the rapid estimation of impurities in alcohol (222). It was used by Mohler, Girard and Rocques for the determination of higher alcohols after the elimination of aldehydes and other interfering substances. Still, today, it constitutes the official method in France for the analysis of fusel oil.

Mohler found that the relative colorations produced by various higher alcohols in concentrations of 0.1% in a 50% ethanol-water solution were as follows (222):

Isobutyl alcohol	10
Amyl alcohols	3
Propyl alcohol	0

The disadvantages of the method are obvious since the amyl alcohols are generally the principal constituent of fusel oil and propyl alcohol frequently exists in noticeable amounts.

Rocques found that by adjusting the ethanol content of the solution to 67.7% the ratio of the coloration intensities between isobutyl alcohol and amyl alcohol was raised to 10:6 instead of 10:3 obtained with 50% ethanol (222).

Several impurities have been found to interfere with the method especially aldehydes and terpenes. It has been pointed out that the resulting color in industrial samples is due largely to the small and variable quantities of furfural naturally occurring in the liquor and, hence, the method fails to furnish a reliable measure of the fusel oil content (240).

In order to separate the aldehydes present in the spirits before conducting the determination of fusel oil, several procedures have been suggested. Mohler treated the spirits with aniline acid phosphate; Girard and Rocques used m-phenylenediamene hydrochloride; while Schidrowitz and Kaye found phenylhydrazine p-sulfonate to be more effective than the latter (222, 240). These substances form non-volatile combinations from which the higher alcohols and the ethanol present can be readily separated by distillation. The most effective method, however, has been found to be that of Fellenberg, which consists of saponifying the spirits in the presence of catalytic silver oxide (210, 222, 240). By this procedure the aldehydes polymerize and the terpenes are decomposed.

With the purpose of increasing the sensibility of the reaction, Saglier suggested the addition of several drops of 0.1% furfural solution to the mixture of spirits and sulfuric acid (222). This author reported the following relative coloration intensities for the various higher alcohols with the addition of 10 drops of the furfural solution to spirits containing 0.1% of the particular higher alcohol at 50% ethanol (222).

Isobutyl alcohol	10.0
Isoamyl alcohol	4.5
n-Butyl alcohol	1.0
Isopropyl alcohol	0.5
n-Propyl alcohol	0

The analytical procedure for the Mohler-Rocques method officially used in France is given by Kervegant as follows (222):

Place in a 250 milliliter round flask 100 milliliters of the spirit to be analyzed previously distilled and adjusted to 50% alcohol. Add 1.0 milliliters of pure aniline, 1.0 milliliters of siropy phosphoric acid and boil gently at total reflux for one hour. At the end of that time,

remove the heat and allow to cool. Provide the flask with an adequate condenser and graduated receiver and distill the solution using sufficient refrigerant to produce a condensate at ambient temperature. Recover in the receiver exactly 75 milliliters of distillate which will contain the totality of the fusel oil and ethanol present in the sample. The recovered distillate will contain 67.7% alcohol. Agitate to render the solution homogeneous. Pipette and mix thoroughly, in a 100 milliliter flask, 10 milliliters of pure sulfuric acid and the recovered distillate of the sample. Simultaneously pipette in another 100 milliliter flask 10 milliliters of the sulfuric acid and 10 milliliters of a standard solution containing 0.667 grams of isobutyl alcohol per liter of ethanol at 66.2%. Place the two stoppered flasks in a calcium chloride bath at 120°C for one hour. At the end of this time the intensities of color obtained are measured in a colorimeter and the fusel oil content determined from a curve.

The French method is subject to serious objections. One of the most important is the lack of sensibility of the method (222). Further, the standard of comparison that is used consists of isopropyl alcohol which does not correspond to the normal composition of fusel oil. Several authors have found results of the order of 25%-50% of the actual fusel oil content (222).

Komarowsky-Fellenberg Method:

Modern colorimetric methods of fusel oil determination utilize the so-called Komarowsky reaction by which colored products are formed through the interaction of higher alcohols with cyclic aldehydes in the

presence of sulfuric acid (225). Numerous chemists have studied extensively the Komarowsky reaction (198, 201, 202, 206, 211, 216, 226, 228, 240, 247, 256). Some of the aldehydes which have been studied include salicylaldehyde, benzaldehyde, p-dimethylaminobenzaldehyde, furfural, veratric aldehyde, and vanillin (240). It has been generally considered, as a result of the work of von Fellenberg, that the higher alcohols are converted by the action of sulfuric acid into unsaturated hydrocarbons, which then combine with the cyclic aldehyde to form colored products (210). Accordingly, substances other than alcohols which could yield unsaturated hydrocarbons with sulfuric acid would interfere. Included in this group are unsaturated hydrocarbons and their derivatives, aldehydes, ketones, acetals, and terpenes, but not acids (240). The most effective method for the elimination of interfering substances is that of Fellenberg in which the sample is saponified with silver oxide as catalyst (210, 240).

As a result of recent investigations, Coles and Tournay have pointed out that apparently the reaction mechanism is more complex than generally accepted because pentene-2, even in high concentration, does not produce a color with p-dimethylaminobenzaldehyde on prolonged boiling. If concentrated sulfuric acid is added to this mixture the color develops only when the acid reaches a definite concentration. He concludes that the acid is necessary for the reaction itself (202).

The general analytical procedure of this method consists of pretreating the sample to be examined for the removal of interfering substances. A measured volume of concentrated sulfuric acid is then added while swirling

the flask in a bath of cold water during the addition. A measured amount of a solution containing the cyclic aldehyde is then added, while still swirling the flask in the cold bath. Simultaneously a second flask is prepared containing a standard fusel oil solution. Both flasks are then placed simultaneously in a bath of vigorously boiling water for a definite length of time. After the end of this period of time the samples are cooled to a given temperature and definite amounts of sulfuric acid are added. The solutions are then ready for comparison in a colorimeter or a spectrophotometer.

As a result of numerous studies of the method, it has been established that a large number of factors would affect the values obtained. The following factors must be controlled (240): (1) amount of sample; (2) nature and amount of reagent; (3) amount of concentrated sulfuric acid; (4) concentration of ethyl alcohol; (5) temperature and time of heating to develop the color; (6) amount of diluent added after terminating the reaction and concentration of sulfuric acid in the diluent solution. Since the reaction is stopped after a definite length of time by chilling the mixture and diluting, it is, therefore, necessary to run standards and samples together under exactly similar conditions. When a spectrophotometer is used for comparing the color developed, the wave length of the light source and the slit opening of the instrument are additional factors to be controlled. In spite of the numerous factors which should be carefully controlled the method is capable of giving accurate, reproducible results and high sensitivity. Besides, it requires shorter times than any other method.

Penniman, Smith and Lawshe have suggested the following analytical procedure as a result of intensive investigations (240):

1. Preparation of the sample: Place 75 cc. of sample in a 500 cc. round bottomed flask. Add 0.5 gram of silver sulfate and 1.0 cc. of (1 + 1) sulfuric acid, and make the total volume up to 110 cc. Reflux gently for 15 minutes. Make the solution alkaline with 5 cc. of a (1 + 1) sodium hydroxide solution and reflux for 30 minutes. Bumping can be prevented by the addition of small quantities of granulated zinc. If foaming occurs, this can be reduced by adding 15 grams of sodium chloride. After the saponification the sample is distilled, 75 cc. of distillate being collected. This distillate contains all of the higher alcohols originally present in the sample. The concentration has been reduced to one-third that of the sample. This reduction in concentration is made necessary by the extreme sensitivity of the color reagents.

2. Procedure for the color reaction with p-Dimethylaminobenzaldehyde or Salicylaldehyde: Place 200 cc. of distillate, obtained as directed above, in a 125 cc. Florence flask. Add 20.0 cc. of concentrated sulfuric acid, swirling the flask in a bath of cold water during the addition. Then add 2.00 cc. of a solution of the reagent in 95% ethyl alcohol (10 mg. per cc.), again swirling the flask in the cold bath.

Prepare a similar flask containing 2.00 cc. of a standard fusel oil solution, acid, and reagent.

Place the flasks simultaneously in a bath of vigorously boiling water. After 20 minutes transfer the flasks to the cold bath. When cool, add 25 cc. of (1 + 1) sulfuric acid and mix thoroughly by swirling. The

solutions are then ready for comparison in the colorimeter.

Coles and Tourney have introduced slight modifications to Penniman's method coupled with the use of a spectrophotometer. It is claimed that they increase the sensitivity of the method about one hundred times and speed up the determination (202).

At the Rum Pilot Plant of the Agricultural Experiment Station of the University of Puerto Rico, a modified procedure has been developed for the color reaction based on the above mentioned methods. Benzaldehyde is used as reagent and the color developed is compared in a 9101-A Beckman Quartz Spectrophotometer, Model DU, Photoelectric, range 320-1000 millimicrons. The method is applied to samples of distillates of fermented molasses. The analytical procedure is as follows:

Pipette 2.0 ml. of the sample into a 125 ml. Erlenmeyer flask and add 20.0 ml. of concentrated sulfuric acid while swirling in an ice-water bath. Add 2.0 ml. of a solution of salycilaldehyde (10 mg. of chemically pure reagent per milliliter of 95% alcohol, U.S.P.), again swirling in the ice-water bath. Treat simultaneously and in identical manner a flask containing a standard solution of fusel oil. Place the flasks for 20 minutes in a bath of water boiling vigorously. At the end of this time transfer the flasks to the ice-water bath. After cooling add 25 ml. of a (1 + 1) solution of sulfuric acid and mix thoroughly by gentle swirling.

Read the per cent of transmitted light as follows:

a. If the fusel oil content of the sample is between 0-90 mg. per 100 ml., use as standard a solution of pure alcohol at 86°P, set the spectrophotometer at a wave length of 560 mu., a slit opening of 0.025 mm., and use the phototube sensitive to ultraviolet light.

b. If the fusel oil content of the sample is between 90-180 mg. per 100 ml., use a standard fusel oil solution of 90 mg. per 100 ml., set the spectrophotometer at a wave length of 600 mu., a slit opening of 0.24 mm., and use the phototube sensitive to infrared light.

The percent of transmitted light is converted into fusel oil concentrations by use of calibration curves prepared using a series of standard fusel oil solutions.

The fusel oil standard used contains 60.0% isoamyl alcohol, 7.0% n-butyl alcohol, 5.0% n-amyl alcohol, 12.0% isobutyl alcohol and 16.0% n-propyl.

The colorimetric methods based on Komorowsky's reaction possesses inherent advantages which could be summarized as follows (240):

1. Much greater speed of determination.
2. The sensitivity is far greater than any other method.
3. By virtue of its sensitivity it is applicable to low-proof beverages such as wines and beers, in which fusel oil was not formerly determined.
4. Two or more color reagents can be used in the case of abnormal or unusual samples.
5. The method yields results of the correct order of magnitude.
6. The accuracy of the results can be greatly increased by using as standard a synthetic fusel oil of similar composition, or actually the same fusel oil as that contained in the unknown sample.

The method possesses the disadvantage that when interfering substances are present, a rigorous pretreatment should be given to eliminate them.

Miscellaneous Methods of Analysis

A rather large number of analytical methods have been suggested from time to time for the quantitative and qualitative detection of fusel oil in spiritous liquids (187, 191, 193, 200, 204, 208, 217, 221, 231, 237, 238, 241, 249, 250, 251, 252, 257, 258, 259, 264). Their use, however, has not been generalized to any considerable extent.

A method which is used in some commercial distilleries for rough plant control is that of salting out the higher alcohols with potassium carbonate. It furnishes results which indicate the order of magnitude of the fusel oil concentration. The method is applied to samples of intermediate plates of the distillation columns to determine the plate of peak fusel oil concentration and the approximate content of higher alcohols in that plate. A procedure which has been used consists of diluting the sample with water to an apparent alcoholic strength of about 25°P by the hydrometer method. A measured amount of the dilute sample is placed in a long graduated cylinder and saturated with potassium carbonate. The height of the upper layer containing the fusel oil is measured in the cylinder and the percent of fusel oil is determined by dividing this volume by the original volume of the sample. Although the upper layer contains substances other than higher alcohols, the error is partially compensated by the fact that some fusel oil remains in solution in the lower layer. It is claimed that with careful manipulation satisfactory results are obtained for some control purposes.

McIntosh gives a method for the qualitative detection of fusel oil in spiritous liquids which consists of agitating 5 cc. of the sample with 6 cc. of water and 15 to 20 drops of chloroform. The chloroform

solution is decanted and evaporated, leaving the fusel oil. It is claimed that about 0.05% may be detected in this manner (237).

The acetylation method suggested by Schicktanz and Etienne is based upon the extraction of the higher alcohols by successive portions of carbon tetrachloride as in the A.O.A.C. procedure (249, 251). The water and ethanol are eliminated from the extract by fractional distillation. The higher alcohols extracted are determined by esterification with acetyl chloride. After the reaction is completed, the excess acetyl chloride is decomposed and titrated. The difference in titer between the sample and a blank allows calculation of the amount of acetyl chloride used in the esterification reaction and subsequently the amount of higher alcohols present. The esterification reaction of the higher alcohols with acetyl chloride, in order to measure quantitatively the fusel oil present, merely substitutes the oxidation step in the A.O.A.C. method. It is pointed out by the authors that any alcohol below butyl alcohol will be excluded from the values obtained (249). It has been found experimentally that in most cases the method gives even lower values than the A.O.A.C. procedure (251).

CHAPTER IV

EFFECT OF THE PRESENCE OF DIFFERENT CONCENTRATIONS OF FUSEL OIL ON THE DETERMINATION OF ALCOHOL BY PICNOMETER, REFRACTOMETER AND HYDROMETER

During the course of operations in a commercial distillery, it is frequently necessary to determine the ethyl alcohol content of samples from intermediate plates of the distillation columns which contain relatively large amounts of fusel oil and smaller amounts of other impurities. It is desirable to make this determination without resorting to time consuming and complicated methods of analysis which are not regularly utilized in daily process control. Determination of the alcohol being removed from the column with the fusel oil side stream and establishing the relation between alcohol and fusel oil compositions along the column are examples of this need.

The methods of analysis most commonly employed in distillery practice for the determination of alcohol are those of Picnometer, Refractometer and Hydrometer. The latter is by far the most used. The methods of Picnometer and Hydrometer are based on the specific gravity of pure alcohol-water solutions at reference temperatures while the refractometer method is based on the index of refraction of pure solutions also at reference temperatures. Obviously, the presence of substances other than alcohol and water will alter the physical properties of the solution, introducing errors in the results obtained with any of the above analytical methods. Fortunately, the amounts of impurities in the raw products of the first columns of the distillation unit and especially in the finished product from the last column are so low that the error

introduced is usually negligible and falls well within the precision limits of the various analytical methods. In the case of aged spirits and finished beverage products, the effect of impurities is minimized by distilling the sample in the laboratory following established procedures before measuring its specific gravity or refractive index. When dealing with samples from intermediate plates of the rectifying column, in which the alcohol content is relatively low while the fusel oil content could be 10 to 20% and in some cases higher, a simple distillation of the sample would be ineffective. Even careful fractionation of the sample would not be satisfactory since a substantial part of the fusel oil would pass into the overhead product if all of the ethyl alcohol present in the sample is to be recovered in the distillate. The difficulties encountered in the separation of fusel oil-alcohol-water by distillation will be discussed in detail in subsequent chapters. With the purpose of providing a method for correcting for the error introduced by the presence of different concentrations of fusel oil at different alcoholic strength, a study was made under the direction of the writer at the Rum Pilot Plant of the Agricultural Experiment Station of the University of Puerto Rico. Solutions of known alcoholic and fusel oil contents were prepared and analyzed for apparent alcoholic content by the methods of Picnometer, Hydrometer and Immersion Refractometer. Solutions containing 200, 500, 1000, 2000, 4000, 7000, 10,000, 15,000, 20,000 and 30,000 milligrams of fusel oil as amyl alcohol per 100 ml. of sample, at 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% alcohol by volume at 60°F were prepared.

Absolute alcohol, reagent grade, was used as the source of ethanol. This alcohol was analyzed in triplicate by the Picnometer method and found to contain 99.25% alcohol by volume at 60°F.

Commercial fusel oil from a Puerto Rican distillery was used as the source of fusel oil. The oil had been concentrated by extraction with water at its origin plant and contained about 60% fusel oil. It was further extracted twice with one-half its own volume each time of water saturated with commercial table salt. After thorough mixing, the mixture was allowed to separate during several hours and the oily upper layer decanted. The oil was then fractionally distilled at atmospheric pressure in a 1" glass column, six feet in height, packed with glass Raschig rings. Portions of 1500 ml. were placed in a 2.5 liter flask and heat supplied through a constant temperature mineral oil bath. The temperature of the oil bath was regulated to maintain an overhead rate of 30 ml. per hour at a reflux ratio of 10:1. The reflux ratio was automatically regulated by an electric timer and a magnetically operated flow divider in the glass column head. The column was maintained at total reflux for a period of two hours before removal of condensate was commenced.

A first fraction of 150 ml., boiling between 83°C and 87°C was discarded to insure complete removal of any ethyl alcohol present. In so doing, water and some of the lower homologues of the higher alcohols were removed.

A second fraction of 1150 ml., boiling between 87°C and 132°C, was collected as purified fusel oil.

A third fraction, consisting of the residue remaining in the flask

was stored apart. After having enough residue, 1500 ml. were placed in the flask and fractionated as before except that no first fraction was discarded. The residue was practically evaporated to dryness at 136°C. The product of this distillation was mixed with the fusel oil fraction collected in the first fractionation. The oil mixture was analyzed in triplicate for specific gravity and fusel oil content giving values of Specific Gravity: $0.8212\frac{25°C}{25°C}$ and 86,665 mgs. of fusel oil as amyl alcohol per 100 ml. The apparent discrepancy of its containing over 100% fusel oil by weight is due to the fact that the fusel oil content is expressed as amyl alcohol while it actually consists of a mixture of alcohols containing appreciable portions of lower molecular weight homologues. These figures are indicative of the high degree of purity of the fusel oil obtained.

The samples were prepared by pipetting previously calculated amounts of purified fusel oil and absolute alcohol into 250 ml., calibrated, volumetric flasks and completing to volume with distilled water. 60 ml. glass picnometers provided with individual thermometer-caps were utilized. The calibration of the hydrometers used was checked with pure water-alcohol solutions of known composition. A Bausch and Lomb Immersion Refractometer with a Type "A" dipping prism, range nD 1.32539 - nD 1.36640 was utilized for measuring the index of refraction of the samples.

The analytical results of this work are presented in Table I, in the Appendix. From them it can be observed that numerous samples were discarded due to the presence of two liquid phase layers. The Refractometer method was employed with samples of an apparent alcohol content

up to 100°P (50% alcohol by volume) at 60°F since that is the upper limit of the scale of the instrument. Dilutions were not made since they would have been equivalent to samples containing lower concentrations of alcohol and fusel oil. The results thus obtained would have been only applicable to identical dilutions in order to account for concentration and contraction effects.

The results show that the differences between apparent and true alcohol content obtained by the Hydrometer and Picnometer methods are almost identical through the range of alcoholic strength and fusel oil content studied. This excellent agreement is to be expected since both methods are based on the specific gravity of the sample. The difference between apparent and true alcohol content by both methods varies with the alcoholic strength at any given fusel oil concentration. At lower alcohol contents the error increases as the alcoholic strength increases and after passing through a maximum it decreases with further increase in alcohol content. With the higher fusel oil concentrations the maximum is not shown since at the lower alcoholic strength partial solubility exists and two liquid phases are formed. This variation is due to the combination of contraction and concentration effects. The error decreases as the alcohol-water content is such that its specific gravity approaches that of the fusel oil. If fusel oil with a specific gravity of $0.8212\frac{25°C}{25°C}$ is added to an alcohol-water solution of that same specific gravity, which corresponds to an alcoholic strength of approximately 185°P, no error would be introduced in the determination of alcohol by the methods of picnometer and hydrometers, should the contraction effects

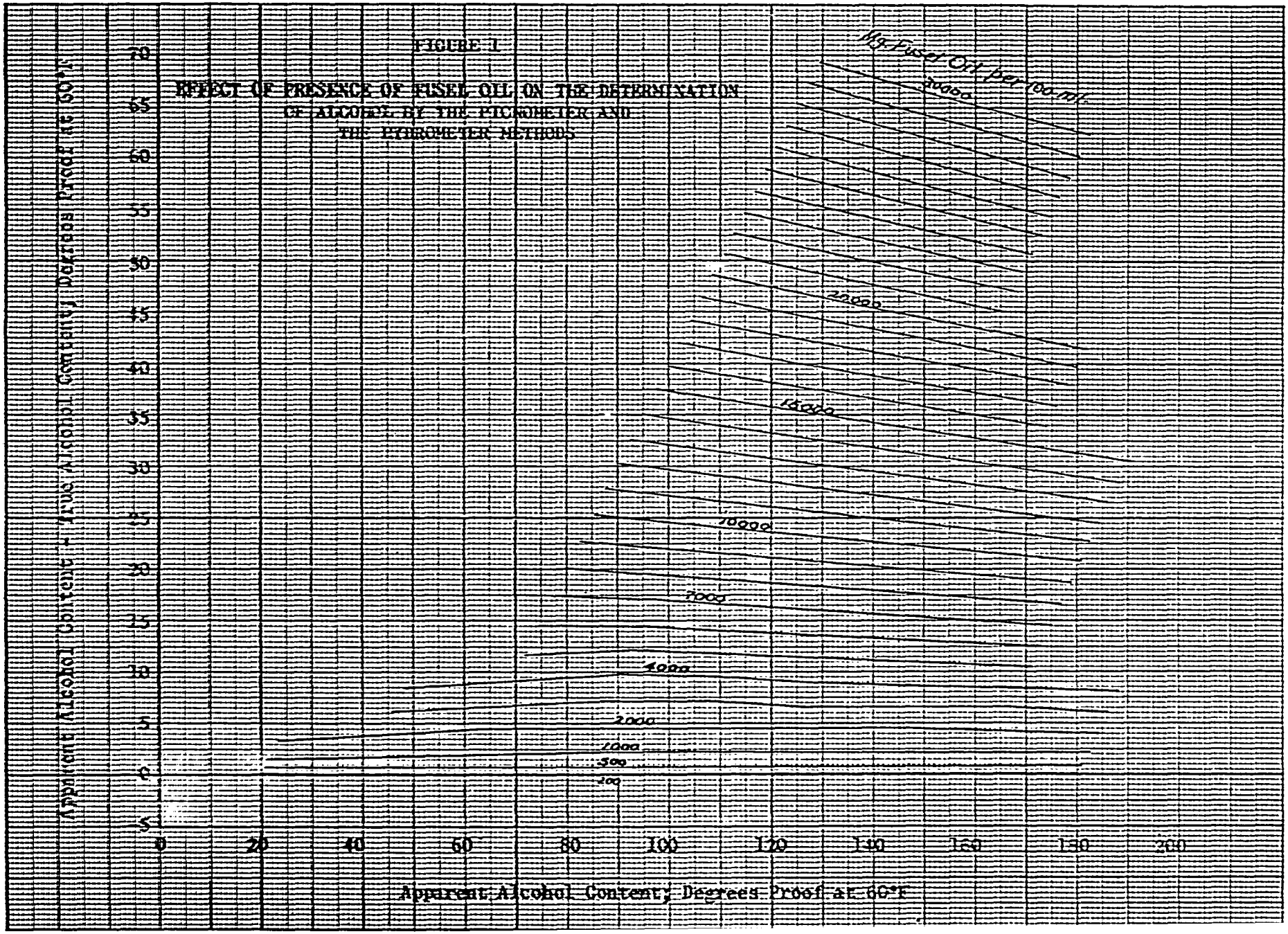
be negligible. Accordingly, at any given fusel oil concentration, the error would tend to decrease as the alcohol content is increased. However, the results obtained indicate that at the lower alcoholic content this effect is more than offset probably by an expansion effect and the error increases with increased alcohol content up to a maximum which depends on the fusel oil content. After this maximum the error decreases with increased alcoholic strength.

The experimental results obtained by the Picnometer method have been plotted in Figure 1. This graph allows rapid determination of the correction to be introduced if the fusel oil content and the apparent proof of the sample are known. The results indicate that at any true alcoholic strength the error produced is directly proportional to the fusel oil content. This fact allows direct interpolation between the lines through experimental points of various fusel oil concentrations. Since, in Figure 1, Apparent Proof as abscissa has been plotted versus (Apparent Proof-True Proof) as ordinate, the points of constant true alcohol content fall on a straight line whose slope is 1.0 when equal scales are used in the abscissa and in the ordinate. In our case the ordinate scale is twice as large as the abscissa scale and, therefore, the slopes of the family of lines of fixed true alcoholic content have a slope of 2. By interpolating along these lines between different fusel oil contents, lines have been drawn in Figure 1 at concentration intervals of 1000 mgs. of fusel oil as amyl alcohol per 100 ml. of sample.

The fusel oil content lines can be extrapolated, if necessary, to cover values of apparent alcohol outside the range covered by the

FIGURE 1

EFFECT OF PRESENCE OF FUSEL OIL ON THE DETERMINATION OF ALCOHOL BY THE PICKNOMETER AND THE HYDROMETER METHODS

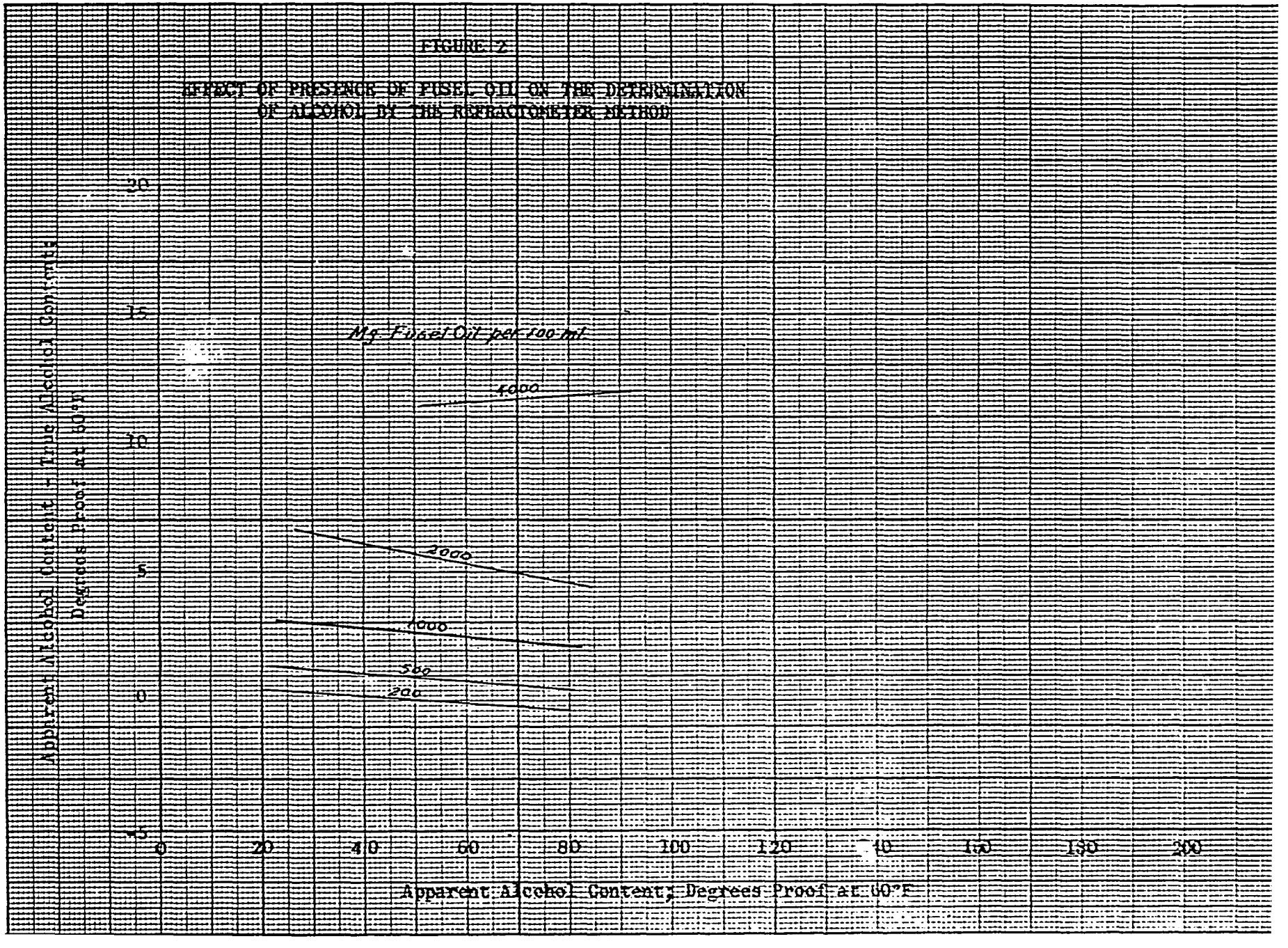


experimental values plotted. It is believed that true alcoholic strengths can be determined with the aid of Figure 1 within an accuracy of 0.5 to 1.0% alcohol by volume at 60°F. A larger size plot would improve the accuracy. Figure 1 can be used for determining correction values for both the Picnometer and the Hydrometer methods since, as was stated above, the experimental values obtained by both methods for the deviations caused by the presence of different concentrations of fusel oil are in excellent agreement.

The experimental results obtained by the Refractometer method are presented graphically in Figure 2. It can be observed that with this method the deviations produced by a given concentration of fusel oil at any given true alcohol content are larger than those produced by the Picnometer and Hydrometer methods. In contrast with the other methods, the error introduced by a given concentration of fusel oil decreases continuously with increasing alcohol content. The line corresponding to a fusel oil concentration of 4,000 mgs. of amyl alcohol per 100 ml. of sample is an exception showing an increase with increasing alcohol content. The results indicate that the same linear relation does not exist between the error introduced and the fusel oil content at a given true alcohol content as was found with the Picnometer and Hydrometer methods. Not enough data is available for plotting lines corresponding to fusel oil concentrations over 4,000 mgs. per 100 ml. Most of the samples prepared at the higher fusel oil concentration fell outside the maximum scale reading of the instrument. In general, more erratic results were obtained with this method. This fact, plus its rather short range of

FIGURE 2.

EFFECT OF PRESENCE OF FUSEL OIL ON THE DETERMINATION OF ALCOHOL BY THE REFRACTOMETER METHOD



application, makes it less useful as compared with the other methods.

Fusel oil concentrations up to 200 mgs. of fusel oil per 100 ml. of sample introduce negligible errors at any true alcoholic strength with the three analytical methods studied.

CHAPTER V

SEPARATION AND PURIFICATION OF FUSEL OIL DURING THE DISTILLATION PHASE OF THE PROCESS OF MANUFACTURE

Objectives of the Distillation Process

Distillation of fermented mashes is one of the most important stages in the process of manufacture of ethyl alcohol by fermentation of substrates. As was indicated in Chapter I, the fermented mash contains minute quantities of a variety of substances in solution, such as inorganic salts and acids, glycerol, alcohols, aldehydes, ketones, esters, organic acids, essential oils and gases, such as carbon dioxide and hydrogen sulfide. In addition, the mash contains solid impurities, consisting in its greater part of nitrogen compounds such as yeast cells, albuminoids and pectic substances which would produce thermal decomposition products of volatile nature when exposed to the temperatures prevailing in the distillation column.

The objective of the distillation process in the manufacture of industrial alcohols is, besides recovering the ethyl alcohol present in the fermented mash, the elimination of impurities to the highest possible extent so that concentrations of the latter in the final product does not exceed established limits. The nature of most of these impurities is such that their presence in the final distillate, even in extremely low concentrations, is strongly evidenced in the odor and flavor of the product.

In the case of alcoholic beverages, it is desirable to retain in the final distillate some of these substances, such as esters and acids, since their presence enhances the quality and the character of the product

while the presence of others detracts from its taste and aroma. The distillation of beverages, thus, becomes a process of selective separation whose objective is the separation from the fermented mash of the ethyl alcohol together with some water and those desirable congeneric bodies which are of utmost importance since it is their characteristic body, aroma and taste that differentiate alcoholic beverages from industrial alcohol (269).

The nonvolatile salts and the suspended impurities present in the fermented mash can be readily removed by distillation. However, the separation of the latter by centrifuging prior to feeding the mash to the distillation columns is a most desirable practice. It has been pointed out by Arroyo that 75% of the foul odor or rankiness which usually accompanies freshly distilled spirits is due to the decomposition by the action of heat of the nitrogenous suspended impurities present in the fermented mash (270). At least some of the products of decomposition are highly volatile passing over with the main product and even when utilizing elaborate and efficient equipment, their complete removal is very difficult.

The volatile impurities present in the fermented mash vary considerably in volatility most of them being less volatile than ethyl alcohol, the exceptions consisting mostly of some esters, aldehydes and acids. Their removal is achieved by the use of adequate rectifying columns. The presence of substances having relative volatilities very close to 1.0 referred to ethyl alcohol, and possibly the formation of azeotropic mixtures, makes the task of completely purifying ethyl alcohol

by distillation a difficult one. In the case of beverages, the selective separation of detrimental impurities, while retaining those which are desirable, makes the process even more complex.

The removal during distillation of fusel oil, which essentially consists of alcohols higher in molecular weight than ethyl, is of great importance since, due to its nature, it is largely responsible for the defects found in industrial alcohols and alcoholic beverages especially those of the lighter types as Puerto Rican and Cuban type rums.

Its separation in the distillation process introduces technical complexities. These alcohols are completely soluble in ethyl alcohol and being less volatile, can be separated by fractional distillation. They are, however, essentially immiscible in water and by the enhanced vapor pressure phenomena, or steam distillation effect, their relative volatilities, referred to ethyl alcohol, are greatly increased beyond 1.0 when low alcohol concentrations are reached in the distillation process. This results in the fusel oil accumulating in fractions of definite alcohol concentration.

It has been pointed out in Chapter I that the amount of fusel oil produced as well as the presence of its various constituents in a given fermentation depends on a number of factors such as kind of substrate utilized, nitrogen source present, nature of the micro-organism utilized, time of fermentation and contaminations present in the mash. This uncertainty in regard to the nature and concentration of the substances present precludes the application of physical chemical methods to predict the distribution of fusel oil in the course of the alcoholic distillation.

Distillation Processes Used Commercially

The distillation processes utilized for the production of alcohol and alcoholic beverages in the fermentation industries can be broadly classified either as intermittent or continuous. Although this work deals mainly with the behavior of fusel oil in the continuous alcoholic distillation from fermented molasses, the main features of the intermittent alcoholic distillation will be discussed in some detail.

Intermittent Distillation Processes

The first processes used for the distillation of fermented liquors consisted of simple distillation and condensation utilizing the intermittent pot-still. The pot-still consisted of a kettle or pot provided with steam coils for heating the mash to be distilled or built in brickwork over a furnace. The still head conducted the vapors directly to a condenser which consisted of a copper coil immersed in a cooling water tank. The kettle was partly filled with the fermented liquid to be distilled and heat was applied either directly under the kettle or through the steam coils. The vapors produced contained not only alcohol and water but virtually all volatile impurities present. As the contents of the pot-still become more exhausted of alcohol, steam distillation effect forces over the higher boiling constituents of fusel oil and other impurities of low volatility. Under normal operating conditions the fermented mash would contain from 5% to 10% alcohol by volume. Accordingly, the distillate obtained by this method would be low in alcohol content. In order to increase the alcoholic strength of the final product, the first distillates were submitted to subsequent simple distillations

until the desired alcohol content was obtained. By the use of cooling coils in the head of the pot-still, which acted as partial condensers or dephlegmators, the rectifying capacity of the still was increased. Improvements in the quality of distillates produced by simple distillation and redistillation were achieved by the separation of "heads" and "tails" fractions rich in lower boiling and higher boiling impurities respectively. The main product thus obtained contained a low portion of the alcohol present in the fermented mash and although relatively purer, its quality was poor compared to present standards.

With the purpose of producing distillates of higher alcoholic strength in a single operation without need of resorting to subsequent redistillations, Pistorius and Adam introduced, in about 1800, the three chambered intermittent distilling still based on the principle of Woulfe's bottle (307, 321). This apparatus consists of a kettle or pot which is partly filled with the fermented mash to be distilled. Heat is applied directly or through steam tubes and the vapors evolved are conducted by an inverted "U" conduit which passes out of the center of the top of the kettle, downward into the bottom of a second vessel. Into this vessel is placed a partially exhausted mixture of heads and tailes used in the previous run. The incoming vapor mixes thoroughly with the liquid and is partially condensed there with the corresponding interchange of heat. The vapors evolved in this vessel, which are richer in alcohol, are conducted in a similar manner into a third vessel containing a mixture of heads and tails fractions obtained during the previous run. The vapors leaving this third kettle, which are relatively strong in alcohol content,

are conducted to a total condenser. In some instances, they are passed through a partial condenser for further enrichment before being lead into the total condenser. The condensate produced at the partial condenser is returned continuously to the last vessel. At the end of each cycle the contents of the third vessel are transferred to the second and provide the partially exhausted liquid for the next operation. The high wines for the next cycle consist of those fractions heavy in impurities which were fractionally separated from the main product as "heads" and "tails" and are added into the last vessel.

The cycle is stopped when the contents of the first and second kettles are exhausted of alcohol while the liquor in the last vessel still contains fairly large concentrations. A great variety of practices have been utilized by different manufacturers regarding the charging of the vessels and the operation of the three chambered still.

Adams analyzed the fractions obtained in several cycles of the commercial operation of a three chambered still and found that the fusel oil present in the fermented mash goes as follows: 4.7% in the heads fraction, 28.9% in the tails fraction and 66.4% in the main product. No fusel oil was found in the alcohol-free slops (268).

Stills of this type produced in one single operation distillates containing 86 to 90% alcohol by weight. A very few of them are still used today in small installations, but their use is generally limited to the beverage industry for the production of heavy bodied distillates which are subsequently blended in rather small proportions to produce special characteristics in the flavor and aroma of the final product.

Modern intermittent stills consist of a plate column provided with a kettle similar to those used in the stills described in the preceding paragraphs. The vapors evolved in this kettle are passed to the bottom of the column by a vapor conduit. The column is provided with total condensers and flow dividers which regulate the flow of reflux to the column. Some authors claim that their use is very desirable for the production of alcoholic beverages, where the separation of impurities is of a selective nature, becoming almost obligatory in the case of heavy bodied types (269).

The use of intermittent distillation columns with a sufficient number of plates and operating at adequate reflux ratios, results in first distillates whose composition is very close to that of the azeotropic mixture. The first fractions would contain also those impurities more volatile than alcohol. The middle fractions usually contain less impurities and are collected apart as high grade alcohol. As the distillation proceeds, the mash in the kettle becomes exhausted of alcohol and richer in water. The steam distillation effect starts forcing up the column those impurities which are partially soluble in water at the operating conditions. Further, the temperature at the kettle increases continuously, and at a certain stage of the distillation process the presence of higher boiling impurities in the main product becomes noticeable. At this point the distillate is collected in separate receivers and these constitute the tails fractions. Only a minor part of the alcohol present in the fermented mash is recovered as high grade alcohol. Robinson and Gilliland give the results of a rectification conducted in a modern intermittent still of a liquor of unidentified origin and such results

indicate that the fraction entitled "High-grade alcohol" contains only 26% of the alcohol present in the original liquor and, furthermore, it is far from being pure alcohol (314). This means that 76% of the alcohol originally present must be submitted to further purification before converting it into high grade product.

The behavior of the fusel oil present during the course of the intermittent distillation will be affected by the nature of its constituents. Should iso-propyl alcohol be present it would appear in the early stages of the distillation process. This probably accounts for the small concentrations of fusel oil found in the first fractions of intermittent distillation processes. As the alcohol content in the kettle is reduced, the higher boiling homologues will start to appear. Adams has indicated that the fusel oil content varies with the proof of the product and maximum concentrations are found in those fractions where the apparent proof is from 132 to 144°P (268). This author has demonstrated with experimental data that the belief of many that fusel oil would be found in the slops from from alcohol is incorrect. All fusel oil present in the original mash appears in the distillate fractions required to remove the ethyl alcohol originally present. Foote has confirmed this fact (281). Several authors have emphasized the dependence of the separation of fusel oil in the distillation process, on the proportions of ethyl alcohol-water-fusel oil present in the liquor to be distilled. Carlson, Smith and Morrell have experimentally measured the volatility of, among other substances, iso-propyl, n-propyl, iso-butyl, n-butyl, 1-Pentanol and 2-Pentanol relative to ethyl alcohol (277). It was shown that all these alcohols are

rendered more volatile than ethyl alcohol after a critical water concentration is reached in each case. As the molecular weight of the alcohol increases, the critical water concentration becomes higher. The approximate critical water concentration for the various alcohols studied is as follows:

Alcohol	Mole % Water
iso-propyl	60
n-propyl	91
iso-butyl	85
n-butyl	93
1-pentanol	91
2-pentanol	86

Unfortunately, no data is given for iso-amyl and active amyl alcohols which are the most important constituents of fusel oil. The volatility of 2-pentanol relative to ethyl alcohol was found to be from 2.2 to 2.7 when the concentration of water was 95.9 mole per cent.

Kervegant reports experimental values determined by Sorel of the vapor-liquid equilibrium constant "K" for iso-amyl alcohol in mixtures with water and ethanol. These results indicate that "K" varies from 0.25 when the concentration of alcohol is 95% by volume to 5.5 when the alcohol content decreases to 25% by volume (290).

Luhder has reported that the volatility of fermentation amyl alcohol, relative to ethyl alcohol, varies from 0.23 when the alcohol content is 95% by volume to 2.07 when the alcohol concentration decreases to 25% by volume (303).

Data on fusel oil distribution under different operating conditions in intermittent distillation processes is virtually non-existent. In the very few cases in which some information is given in the literature with

regard to fusel oil content of various fractions, there is no information as to the actual operating conditions such as reflux ratio and number of plates in the column utilized in the fractionation (268, 291, 314).

Continuous Distillation Process

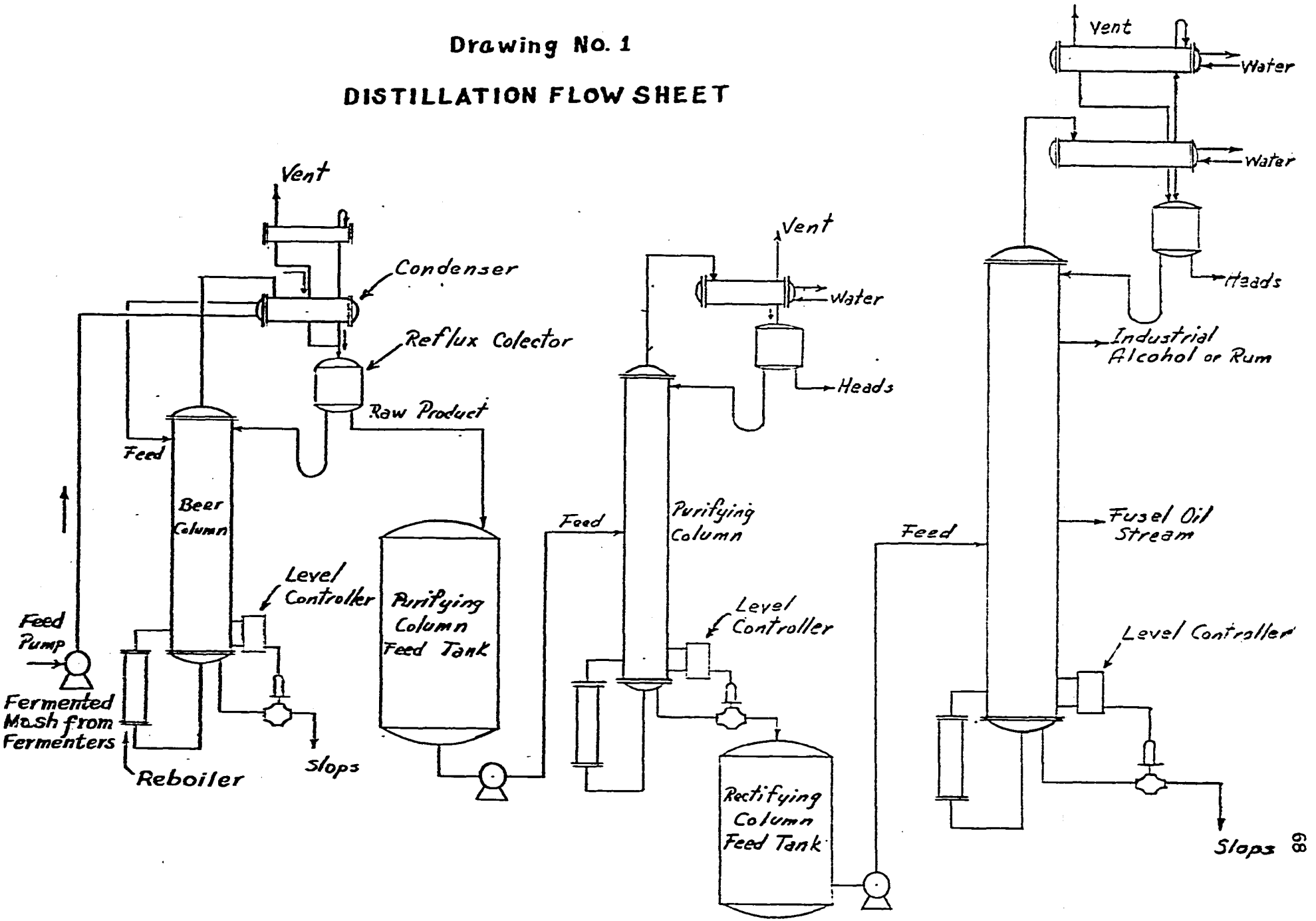
In modern practice, continuous distillation processes have substituted almost entirely the older intermittent methods. Since they are especially well adapted for mass production, continuous stills introduce a number of advantages of economic nature. Their compactness, floor space economy, high unit capacity, savings of time, manipulation and fuel are among the most important. Further, the ability to produce neutral spirits of greater purity have generalized their use in the alcohol industry. Intermittent stills are presently used to a minor extent in the beverage industry. For the manufacture of light type beverages, such as Puerto Rican and Cuban rums, continuous stills are utilized almost exclusively.

Modern continuous distillation units consist of at least three columns. A flow diagram of the operation of such a unit is presented in Drawing No. 1.

The first column, known as the "Beer" or "Exhaustive" column, has as its chief function the removal of all the alcohol present in the fermented mash. The largest part of the column is accordingly a stripping section containing 15 to 25 sieve plates for suitable handling of a solids containing stream. The upper section of the column has a small number of bubble-cap plates and these are usually separated from the stripping section by an impingement plate, whose function is to prevent solids from

Drawing No. 1

DISTILLATION FLOW SHEET



entering the top of the column. Slops consisting of water with dissolved and undissolved solids flow from the bottom of the tower. This stream can be further processed for cattle feed and yeast recovery if previous centrifugation of the fermented mash is not practiced. Alcohol vapor of 80-130 proof strength, containing volatile impurities, leaves the top of the column where it is condensed and divided between reflux and top product streams. Reflux ratios between 0.5:1 and 2:1 are generally used. The beer column product, designated as raw distillate or raw product, passes to receiving and measuring tanks which at the same time serve as feed tanks for the purifying column, which is the next stage in the distillation processes. Water may be added to the beer column product in the receiving tanks to realize any desired concentration in the purifying column feed, usually from 40 to 100 proof. In some installations the vapors from the top of the beer column pass to a partial condenser where just enough vapors are condensed to supply the reflux stream, the rest being fed to the purifying column. The method of totally condensing the vapors and feeding the purifying column in the liquid phase is more favored in industrial practice since its greater flexibility and ease of control, resulting in a more uniform product, more than offsets the additional expense of fuel and condensing water. Feed is added in the middle section of the purifying column.

The function of the purifying column, which usually contains from 30 to 55 bubble-cap plates, is to remove "heads" consisting of low boiling constituents. These are removed with the overhead product which may contain up to 10% of the ethyl alcohol fed to the column and whose

composition is very close to that of the alcohol-water azeotrope. The vapors from the top of the column are condensed and are divided into reflux and product streams. Very high reflux ratios are utilized in commercial practice. The writer knows of cases in which ratios of 50:1 and 100:1 are used. The "purified" alcohol-water solution passes from the bottom of the column to receiving tanks which serve as feed tanks to the rectifying column. Actually the term "purified alcohol" used in industrial practice is far from being true since the higher boiling impurities present in the raw product from the beer column are still present.

The alcohol bottoms of the purifying column are fed into the middle section of the rectifying column which usually contains from 40 to 75 bubble-cap plates. The purpose of the rectifying column is to concentrate the alcohol to the desired strength and to remove remaining impurities and additional impurities formed during rectification. Here again, "heads" are removed from the top of the column. The top vapors pass to the condensers and the condensate is divided into reflux and "heads". Normally, the "heads" product contains a smaller percentage of the alcohol fed to the column than in the case of the purifying column. Alcohol or beverage product of the desired strength is removed as a liquid side stream from the upper trays of the column. Main products removed as side streams are known as "pausterized" products. Reflux ratios, expressed as the ratio of the outside reflux stream to the main product side stream of 3:1 to 5:1 are commonly used. In some cases higher values are utilized. Alcohol-free slops, consisting of water and higher-boiling water soluble impurities are removed. The fusel oil accumulates in the

intermediate plates of the column and is removed as a liquid side stream a few plates above the feed plate. This stream passes into fusel oil receivers where it is cooled and generally diluted with water which causes the fusel oil to separate into a concentrated, oily, upper layer. The oil is decanted and the lower layer is returned to the process for recovery of the ethyl alcohol present. It is usually utilized to dilute the raw product from the beer column.

The process just described constitutes the core of modern continuous alcohol distillation processes although numerous modifications and refinements are in use today.

Unger has reviewed advances in alcohol distillation methods (324). The operation of the beer column under vacuum at low temperature was suggested in order to reduce thermal decomposition of mash constituents which are largely responsible for unpleasant and objectionable flavor and aroma of the product. This problem is more successfully and economically eliminated by centrifuging the mash continuously before feeding it to the beer column.

One of the most important and successful recent improvements consists of operating the purifying column as an extractive distillation column with the addition of water at the top. A rather complete elimination of impurities is achieved. In some instances, both an extractive distillation and a conventional purifying column are used in series (324). The operation of the extractive distillation column is discussed in later paragraphs.

In some instances the "heads" from the purifying and rectifying columns are chemically treated and redistilled in a separate batch column

taking heads and tails off and yielding second class spirit (324). Unger further reports that at Joseph E. Seagram and Sons the "heads" products are fed to a continuous 75 plate column where they concentrate to 1-2% acetaldehyde and 10-20% ethyl acetate in a stream equivalent to 0.1% of the total product. The recovered alcohol is recycled. Operating details for the above processes are not available in the literature.

In some plants, fusel oil streams are presently washed countercurrently in continuous packed extractive columns. A fusel oil rich layer separates in the upper part of the column and is removed continuously as fusel oil by-product. In other instances fusel oil streams are further processed in continuous columns of 50 to 60 plates from where fusel oil and high boiling esters are obtained (324).

Kirk and Othmer describe a number of alcohol distillation units of increasing degree of refinement and complexity (294).

Behavior of Fusel Oil in the Operation of the Purifying Column

The raw product to be fed to the purifying column contains most of the volatile components present in the fermented mash. The higher alcohols content in it generally varies from 100 to 1100 milligrams of fusel oil as amyl alcohol per 100 ml. of pure alcohol. In the case of light type rums, in which special yeast strains are used, its concentration can be even lower.

The dilution of the raw product with water before feeding to the purifying column aids in the separation of impurities in said column. The volatility of most impurities relative to alcohol is greatly increased at reduced ethyl alcohol concentrations. The amount of dilution

used is limited by economic considerations since it requires increased column capacity and greater expense of steam. The direct introduction of steam into the still, when used, produces an additional diluting effect on the bottoms of the column. In modern practice, however, the use of surface evaporators as reboilers is to be preferred since the use of open steam might result in the introduction of impurities, such as fractions of lubricating oils, which would appear in the final product detracting from its quality.

Since a small percentage of the alcohol present in the feed is removed in the "heads" product, the alcoholic strength of the bottoms from the purifying column is very close to that of the feed when closed steam is used. Accordingly, the alcohol concentration from the feed plate to the bottom of the column decreases but little. Further, due to the presence of a hydrostatic head gradient which increases toward the bottom end of the column, and to the small alcohol concentration gradient existing in the opposite direction, the temperatures prevailing in the plates of the column under steady operating conditions show a gradient which increases toward the bottom of the column and reaches a maximum at the reboiler. Consequently, the solubility of fusel oil in the liquid phase of the plates of the stripping section of the column is not greatly altered with the result that no significant steam distillation effect occurs. The distribution of concentrations of fusel oil along the stripping section is rather uniform. The bottoms contain essentially all the fusel oil entering with the feed and consequently there is no tendency for any strong accumulation of fusel oil in the intermediate plates of

the column. Barbet's diagram, given by Robinson and Gilliland, shows that the fusel oil concentration in the bottoms of a purifying column is only slightly higher than that of the feed (314). This is caused by the fact that essentially all fusel oil entering with the feed would go into the bottoms whose volume per unit time would be somewhat smaller than that of the feed. The difference corresponds to the volume of the "heads" product which, in turn, are low in fusel oil content. Barbet's data also confirms that the distribution of fusel oil along the stripping section of the column is rather uniform.

Several flow diagrams of continuous alcohol distillation processes found in the literature indicate that fusel oil side streams are removed from intermediate plates of the purifying column where accumulations are supposed to occur (265, 266, 310, 313). Unfortunately, operating conditions are not given. No information is available regarding the addition of water or direct addition of steam which would produce a reduction in the alcoholic concentration in the lower plates of the column to the extent of producing the enhanced vapor pressure phenomena with the corresponding removal of fusel oil from the bottom product and its accumulation in intermediate plates.

In order to confirm Barbet's results and the theoretical considerations exposed above, two experiments were conducted by the writer utilizing the facilities of the Rum Pilot Plant of the Agricultural Experiment Station of the University of Puerto Rico. The purifying column of its distillation unit contains 40 bubble-cap plates of 8" nominal diameter and a plate spacing of 10". The overhead vapors are condensed in a total

condenser and pass to a reflux collector. From this collector the condensate is divided into reflux and "heads" streams by means of automatic flow rate controllers which allow the setting of any desired reflux ratio. A thermometer bulb installed in the path of the reflux stream regulates the inlet of condensing water to the total condenser to maintain any desired temperature in the reflux. The total condenser is vented through a vent condenser which condenses any vapor passing over with the non-condensable gases and returns the condensate to the reflux collector. Atmospheric pressure prevails in the top plate of the column during operation. Steam for heating is added into the shell side of an outside, vertical, tubular heat exchanger which constitutes the reboiler of the column. The boil-up rate is controlled by means of a differential pressure controller with taps near the top and bottom ends of the column. In order to maintain constant any set differential pressure, the controller resets an automatic steam flow controller which in turn regulates the supply of steam to the reboiler. The feed rate to the column is also regulated by an automatic flow controller. A feed-heater provided with an automatic temperature controller maintains the temperature of the feed at any desired value. The flow of bottoms-product off the column is regulated by an automatic level controller installed in the bottom of the column. The automatic flow controllers used to regulate the flow of feed and products to and from the column could be operated, if desired, in conjunction with a temperature controller which would reset one stream flow controller to maintain a constant reference temperature at a given point in the system. Next chapter presents a detailed discussion on

automatic control systems for the continuous alcoholic distillation. The control system utilized for these experiments consisted of manually re-setting the feed flow controller to maintain constant a reference temperature in the plate above the feed plate.

Every plate in the column is provided with taps which could serve as a temperature well. Fifteen thermocouples are installed along the column for measurement of temperatures. A large number of plates have been manifolded for addition of feed and withdrawal of side streams, if desired. All plates are provided with sample outlets.

Feed compositions of 30% and 40% alcohol by volume were studied. Similar reflux ratios, boil up rates and per cent of alcohol in feed going into "heads" were utilized. These figures were 25:1, 10.4 gallons per hour and 3%, respectively. Plate 16, from bottom up, was the feed plate in both experiments.

The rates of flow of the feed, reflux and "heads" streams for the experiment with the 30% alcohol feed were respectively 40.0, 10.0, and 0.4 gallons per hour. The corresponding figures for the experiment with the 40% alcohol feed were 33.3, 10.0 and 0.4 gallons per hour. The reference temperatures maintained constant in the vapor space of the plate above the feed plate were 183°F for the 30% alcohol feed and 186°F for the 40% alcohol feed. The column was maintained at total reflux of 10.4 gallons per hour until enough accumulation of alcohol in the column occurred to bring the reference temperature to the desired value. At that moment withdrawal of "heads" product was commenced and the reflux stream adjusted to 10.0 gallons per hour. Samples were taken from plates 40, 38, 35, 32, 29, 26, 23, 20, 17, 14, 11, 7 and 3 at 0, 8, 16 and 24 hours after removal

of "heads" product began.

The results of these experiments are presented in Tables 6 and 7. These data confirm the results obtained by Barbet. There is no significant accumulation of fusel oil in the intermediate plates of the purifying column when operating by conventional methods and utilizing closed steam. The fusel oil content of the bottom product of the column is slightly higher than that of the feed. The fusel oil content in the top plates is somewhat higher than expected. This is probably due to the presence of iso-propyl alcohol in the fermented molasses mash and consequently in the distillate from the beer column. At fusel oil concentration in the "heads" of 25 mgs. of fusel oil per 100 milliliters of sample, the fusel oil removed in the "heads" is equivalent to about 0.5% of the fusel oil present in the feed. The data presented in Chapter I on compositions of fusel oil from different sources indicates that fusel oil originating in fermented sugar cane molasses usually contains above 0.6% of iso-propyl alcohol.

The results obtained lead to the obvious conclusion that no fusel oil side-stream should be withdrawan from the purifying column when utilizing conventional methods of operation and closed steam. Modifications to the conventional operating procedure which would result in producing considerable decrease in alcohol content at the lower plates of the column while maintaining high alcoholic strengths in the top plates, would produce accumulations of fusel oil in the intermediate plates. These could be accomplished only if a large per cent of the alcohol in the feed were taken in the overhead product and by diluting with water and open steam

TABLE 6

FUSEL OIL AND ALCOHOL DISTRIBUTION BY PLATES IN PURIFYING COLUMN

Feed - 80°P; Reflux Ratio - 25:1

Fusel Oil Concentration Given as mgs. of Amyl Alcohol per 100 ml. of Sample
Alcohol Content Given in Degrees Proof at 60°F

Time of Sampling	0 hrs.		8 hrs.		16 hrs.		24 hrs.	
Plate	Fusel Oil	Alcohol	Fusel Oil	Alcohol	Fusel Oil	Alcohol	Fusel Oil	Alcohol
40	25	189.7	30	190.0	40	190.0	40	190.1
38	20	189.1	25	189.6	25	189.7	35	189.7
35	20	188.1	25	188.7	20	188.7	30	189.0
32	25	186.8	25	187.3	25	187.3	25	187.5
29	40	184.2	30	185.3	25	185.4	25	185.6
26	50	181.2	45	182.1	35	182.7	30	182.7
23	20	177.2	55	177.6	40	177.8	40	178.0
20	55	171.3	70	171.1	60	171.7	45	171.3
17	75	87.3	70	87.8	70	89.5	45	87.5
14	90	80.2	85	79.7	80	79.0	45	79.2
11	75	79.2	85	78.7	85	79.7	45	79.0
7	100	79.0	90	78.7	85	79.6	50	79.3
3	---	79.3	110	79.0	95	78.7	60	79.1

	Fusel Oil	Alcohol
Composite Sample of Feed	70	82.3
Composite Sample of Heads	35	189.9
Composite Sample of Bottoms	75	79.5

TABLE 7

FUSEL OIL AND ALCOHOL DISTRIBUTION BY PLATES IN PURIFYING COLUMN

Feed - 60°P; Reflux Ratio - 25:1

Fusel Oil Concentration Given as mgs. of Amyl Alcohol per 100 ml. of Sample
Alcohol Content Given in Degrees Proof at 60°F

Time of Sampling	0 hrs.		8 hrs.		16 hrs.		24 hrs.	
Plate	Fusel Oil	Alcohol	Fusel Oil	Alcohol	Fusel Oil	Alcohol	Fusel Oil	Alcohol
40	--	189.4	20	189.6	30	190.0	30	190.0
38	5	188.4	20	188.9	25	189.4	30	189.5
35	5	187.6	15	188.5	20	188.5	30	188.6
32	20	185.1	30	186.5	35	186.6	30	186.8
29	25	182.2	45	183.3	30	183.6	35	182.7
26	35	179.7	65	179.1	35	179.2	65	179.5
23	55	174.0	80	174.6	35	174.9	75	173.9
20	95	160.6	170	161.3	95	162.7	160	161.3
17	40	68.3	50	72.3	60	67.6	65	67.8
14	45	59.8	70	59.6	65	59.0	75	60.3
11	65	59.8	75	59.6	85	59.0	85	59.0
7	65	59.6	85	59.7	85	59.3	70	59.6
3	60	59.5	95	59.4	95	59.3	95	59.4

	Fusel Oil	Alcohol
Composite Sample of Feed	40	60.1
Composite Sample of Heads	30	--
Composite Sample of Bottoms	50	58.6

the lower plates of the column. Since fusel oil can be very effectively removed in the rectifying column or by operating the purifying column by the extractive distillation method to be described in the next paragraphs, no need is found for the economic burden of separating large amounts of alcohol in the "heads" which would have to be reprocessed to recover the ethanol and convert it into first class product.

Objections to the use of open steam are based, as mentioned before, on considerations of the quality of the final product. Its use, however, would produce significant dilutions in the bottom product. There is no fusel oil distribution data in the literature for such cases. Some accumulation along the column should be expected. However, since the presence of small quantities of ethyl alcohol greatly increase the solubility of fusel oil in water solutions, its extent is uncertain and would depend to a high degree on the particular operating conditions.

It was mentioned in previous paragraphs that one of the most successful modern modifications of the conventional continuous distillation process is the operation of the purifying column as an extractive distillation column utilizing water as the extractive agent. This process is based on the principle that at reduced alcohol concentrations most impurities present in the raw distillates become more volatile than ethyl alcohol. Accordingly, water is added in the top plate of the column to produce a decrease in alcohol concentration through the column. The low concentration of alcohol obtained in the bottom of the column forces the impurities off the bottom product. Much lower alcoholic strengths are produced also in the vapor leaving the top of the column

due to addition of water in the top plate and to the use of less plates in the enriching section by feeding at a higher plate. Economic considerations indicate the convenience of adding the minimum amount of water required for effective purification. Otherwise excessive column capacity and steam consumption would be required in the following stage of the process. Data available in the literature on the operating conditions of this process are meager.

Interesting results have been obtained by the writer on preliminary experiments designed to establish optimum conditions for the purification of raw distillates from fermented molasses. The same purifying column described above was utilized.

In one experiment a raw distillate was diluted to about 100°Proof and fed to the column at plate 15. Water at 202°F was added in the top plate of the column in sufficient amounts to yield a bottom product of about 30°P. The analytical results of composite samples of the feed, "heads" and bottom product of the column are given below. The acids, aldehydes, esters and fusel oil concentrations are expressed in mgs. of acetic acid, acetaldehyde, ethyl-acetate and amyl alcohol, respectively, per 100 ml. of sample. The alcohol content is expressed in degrees proof at 60°F.

	Aldehydes	Esters	Acids	Fusel Oil	Alcohol
Feed	15.5	32.0	0.6	90	98.1
Heads	470.5	183.0	1.4	2000	75.7
Bottom Product	1.6	0	0	20	33.2

In a second experiment the same feed was diluted to 40°P and fed at plate 32 of the column. Water at 202°F was added at the top plate

to produce a bottom product of about 10°P. The analysis of the bottom product obtained was as follows:

Aldehydes	0.8
Esters	0.0
Acids	0.0
Fusel Oil	0.0
Alcohol	11.3

These experiments were of an exploratory nature. The data obtained, although incomplete and requiring confirmation, indicates that this process is very effective. Completion of these studies is planned for the near future.

As is inferred from the results presented above, this method of operation would not be suitable for the production of alcoholic beverages since it results in a complete elimination of all congeneric substances present in the raw distillate resulting in a neutral mixture of ethyl alcohol and water in which the substances responsible for the characteristics and quality of genuine beverages are absent.

Behavior of Fusel Oil in the Operation of the Rectifying Column

The alcohol bottoms from the purifying column are fed to the rectifying column where, besides concentrating the alcohol to the desired alcoholic strength, remaining impurities are eliminated as well as those formed in the column during the rectification process. The enriching section of the column usually contains from 30 to 50 plates. The top distillate composition is very close to that of the alcohol-water azeotrope which is 95.58% alcohol by weight. A small stream containing 2% to 5% of the alcohol fed to the column is removed as heads. The main product is removed as a liquid side-stream several plates below the top

plate. By this procedure the content of low boiling impurities in the main product is reduced to a minimum. The concentration of these impurities increases successively toward the upper end of the column and reaches a maximum concentration in the overhead distillate.

The bottom product of this column consists of water and water soluble impurities. The concentration of alcohol in the intermediate plates varies between zero and the azeotropic composition.

Fusel oil is completely soluble in ethyl alcohol and, being less volatile, it is forced down the column by rectification. As the oils pass down to the bottom, they become immiscible in the higher water concentrations and steam distillation forces them to rise. Not being able to escape, due to the two opposing effects, by either end of the column, the fusel oil accumulates at some intermediate plates. The location of the plate of maximum accumulation and the distribution of fusel oil along the column are functions of such variables as reflux ratio utilized, alcohol content in the feed and number of plates. During the first hours after a distillation run is started, fusel oil is permitted to accumulate until a given concentration is obtained in the plate of maximum accumulation. At this point, withdrawal of the fusel oil side-stream is commenced. The volume of the side-stream should be such as to produce a material balance between the fusel oil entering with the feed and that leaving with the main product, the "heads" and the oil side-stream itself. The maximum fusel oil concentration allowed in the plate of greatest accumulation depends on the specified content of fusel oil in the main product. Should the fusel oil side stream not be withdrawn, the higher alcohols will continue to accumulate in the column with

a corresponding increase in the fusel oil content in the main product. This accumulation will continue until a fusel oil content in the main product is reached which produces a material balance between the oil entering the column with the feed and that leaving in the various streams.

If in the course of normal operation the fusel oil content in the feed varies, there will be either an increase or a depletion of the fusel oil accumulated in the column until such concentrations are obtained at the plates from which the fusel oil side-stream and the main product are being removed that produces the required oil balance in the column.

In actual distillery operation in the manufacture of industrial alcohol and alcoholic beverages, it is necessary on some occasions to alter the operating conditions of the purifying and rectifying columns due to variations in the quality of the fermented mash and consequently in the raw distillate from the beer column. Further, in the production of alcoholic beverages it is a common practice to produce distillates of different characteristics under different operating conditions which, after aging, are properly blended to produce a well balanced product. Very often public preference forces manufacturers to alter the characteristics of their product which in turn requires alterations in the conditions of operation in the distillation phase of the process. As an example of this it may be mentioned that in line with the increasing trend toward the consumption of light type beverages in the United States, several manufacturers of medium and heavy bodied rums in the Caribbean Area have been forced to modify their former processes of operation, in some cases involving rearrangement of the complete distillation unit, in

order to supply the new market demands.

There is no published data on fusel oil distribution along the rectifying column under different operating conditions. Again, as for the case of intermittent distillation processes, due to uncertainties regarding the constituents of fusel oil present and their respective concentrations in any specific case, no attempt has been made to predict its distribution by theoretical considerations.

Availability of distribution data under different operating conditions would help the operator in the selection of the latter. These data would assist in establishing the plate from which the main product should be withdrawn. It would also indicate the plate of maximum concentration from which the fusel oil side-stream should be removed. It would indicate what maximum concentration could be permitted on the plate of maximum accumulation without surpassing the specified limit of fusel oil content in the main product. Operation at the highest allowable concentration of fusel oil in the plate of maximum accumulation would be advantageous since a smaller fusel oil side-stream would be required to maintain a material balance between the fusel oil entering the column with a given feed and that leaving with the products. Smaller and richer fusel oil streams would represent smaller losses in ethyl alcohol. In large factories where the fusel oil is subjected to further processing for the recovery of ethyl alcohol and for increasing the concentration of higher alcohols in the final fusel oil by-product, the handling of a smaller and richer fusel oil stream would represent savings in the costs of operation and in equipment investment.

In the design of commercial distillation plants, fusel oil distribution data should be examined before establishing the required reflux ratio for a given product specification. The reflux ratio in turn will determine the diameter of the column for a given output capacity. Besides being used in predicting the plates from which the main product and the fusel oil side-stream should be withdrawn, it would provide a basis for estimating the amount of fusel oil stream to be produced and the concentrations of ethyl alcohol and fusel oil in it. This information, in turn, will be the basis for the design of the ethyl alcohol recovery unit. At present design of this equipment is based on highly empirical methods.

The absence of distribution data under different operating conditions results in the utilization in most cases of empirical methods of operation which either yield products of low quality or involve the separation from the process of very large "heads" and fusel oil cuts. The latter results in excessive losses of ethyl alcohol or in the need for extensive re-processing of by-product streams or both.

Robinson and Gilliland present a set of distribution data credited to Barbet (314). The operating conditions, however, are not given in full. There is no information regarding the reflux ratio utilized and the values for the various streams. According to this data, peak concentrations of fusel oil occur in two different plates requiring the withdrawal of two different side-streams. The upper point of maximum accumulation falls in the fourth plate over the feed plate while the lower corresponds to the sixth plate below the feed plate. The information

is contradictory regarding the nature of the higher alcohols present at each of the two plates of peak concentration. The concentration diagram presented indicates that the upper accumulation consists of those alcohols more soluble in water while the lower portion is formed by the most insoluble ones such as amyl alcohol. The text, however, says that the oils less soluble in water collect higher up in the column than those more soluble. In the operating conditions given it is specified that the alcohol content in the feed is 40% by volume. The concentration chart indicates that the alcohol content in the liquid phase of the feed plate is 80% by volume. Should the feed have been added at the plate containing 40% alcohol by volume, it seems that the maximum accumulation would have been produced at some point above the feed plate. Further, it is believed that the dilution effect of the feed, which contains less fusel oil than the liquid on the plates, may have produced the region of lower fusel oil concentration between the two peaks. In industrial practice the oil stream is normally withdrawn from a single point above the feed plate. According to the concentration diagram and the information given in the text, the ratio of fusel oil concentrations between the feed and the liquid in the two plates of peak concentration is of the order of 4:1. Data found in the literature and the experimental results presented in Chapter VII indicate that ratios of the order of 100:1 and higher are obtained in commercial practice (280). According to the information given, the fusel oil content in the raw distillate from the beer column is 2 grams per hectoliter of liquor containing 50% alcohol by volume which corresponds to 2.0 milligrams per 100 milliliters of raw product

or approximately 0.004% of the absolute alcohol present. The range of composition of fusel oil in the raw distillate, however, is usually from 0.1% to 0.7% of absolute alcohol or 25 to 175 times higher (316, 324). The fusel oil concentration given for the liquid in the plates of maximum accumulation is about 15 grams per hectoliter or 15 milligrams per 100 milliliters. The concentrations obtained in practice are usually 500 to 1200 times greater.

According to the concentration diagram, the apparent alcohol content of the plate where the upper peak concentration falls, is about 172°P. Again this is in discrepancy with the results found in practice which indicate that fusel oil accumulates in the range of 132-144° apparent proof (316, 322, 324).

Fertman, Pokrovskii and Uishnevskaya have studied the fusel oil content by plates of a distillation column being operated by a process which departs from conventional continuous distillation (280). Although the original article does not describe the distillation process used nor give the values of the operating variables, it can be inferred that the column is installed over a kettle and the feed is added, apparently in a continuous manner, during the first portion of the operating cycle. Further, the fusel oil content by plates is reported as per cent by volume of absolute alcohol present but the alcohol content by plates is not given.

In view of the lack of data on fusel oil distribution under different operating conditions and its potential value in the design and operation of continuous distillation units, it was decided to conduct a series of experiments at different feed compositions and reflux ratios

covering the normal range of operation found in commercial practice. The results of these studies are presented in Chapter VII.

Purification of the Fusel Oil Take-Off

The fusel oil stream, as removed from the rectifying column, contains rather large concentrations of water and ethyl alcohol and a small per cent of high boiling substances such as fatty acids and esters. Data available in the literature and the results presented in Chapter VII indicate that the higher alcohols content in the run-off usually varies between 7.0% and 20% by weight (280). The content of impurities is of the order of 0.1% to 1.0%. Large plants with efficient equipment and control methods should be able to operate steadily close to the upper limit and even at a somewhat higher concentration. Smaller installations with less efficient equipment, and very often lacking adequate control systems and technical supervision, produce fusel oil streams containing fusel oil concentrations much lower than 7.0%. Based on the results of Chapter VII, and neglecting the content of higher boiling substances, a typical composition by weight for fusel oil take-off from molasses origin could be given as follows:

Higher alcohols	12%
Ethyl alcohol	47%
Water	41%

The apparent proof of such a mixture would be about 135°P at 60°F.

In industrial practice the fusel oil stream is processed to recover as much as possible of the ethyl alcohol contained in it. In larger installations the fusel oil fraction is further purified until required specifications are obtained for industrial purposes. In smaller plants,

especially those located in lands far removed from industrial centers, the enriched fusel oil produced, which still contains some alcohol and water, is generally discarded. Numerous apparatus have been described in the literature for the separation and purification of fusel oil (267, 271, 272, 274, 286, 293, 300, 305, 309, 316, 317, 322). Generally these apparatus, although differing in specific design features, basically consist of devices which cool the fusel oil stream and bring it in contact with cold diluting water in such proportions as to produce almost complete separation of the higher alcohols into an oily, upper layer which is decanted. Ullmann reports that by diluting to 15% alcohol by volume, the fusel oil separates readily (320). Much lower alcohol concentrations are used in many cases. Successive extractions with water reduce the alcohol content and increase the concentration of higher alcohols in the fusel oil by-product (276). Apparatus for use with continuous and intermittent distillation units have been devised. Modifications of the conventional method involve removing the fusel oil take-off in the vapor phase and bubbling it through cooling water (271, 286).

Data is available in the literature on the analysis of enriched fusel oils from numerous sources which indicates different degrees of enrichment (273, 288, 302, 311, 312, 316, 323). Water content varies from about 6% to 20% while ethyl alcohol varies from about 1% to 17%.

Various methods have been used to enhance the separation of alcohol and water from fusel oil by-products. Saturated solutions of sodium chloride, potassium carbonate, calcium chloride and other salts, instead of water have been used in industrial practice (284, 295, 322).

Krasnitskii has patented a method in Russia in which it is claimed that by introducing a solution of sodium chloride into the fractionation tower, the separation of fusel oil is improved (295).

Kiefer has patented, in this Country, a distillation apparatus, consisting of two continuous packed columns, for converting low proof wash containing fusel oil into high proof ethyl alcohol (293).

Swallen and Tindall have patented a process for the purification of either grain or molasses fusel oil, which involves bringing the crude fusel oil, in the presence of certain amounts of either sulfuric or phosphoric acids, into contact with an ester of amyl alcohol having a boiling point substantially higher than that of the fusel oil to be treated (318). The ester should be present in sufficient amount to retain the impurities present in the fusel oil, the latter being removed by distillation at a temperature which is approximately equal to or slightly above the boiling point of amyl alcohol, but substantially below the boiling point of the ester. Amyl phthalate, stearate, borate and phosphate, among others, may be used.

Continuous fusel oil washers are used in modern distillation units (294). In these apparatus, the fusel oil take-off is extracted countercurrently with water in a packed column which is provided in the top with disengaging section from where the concentrated fusel oil upper layer is decanted.

In another process described in the literature, the fusel oil streams, removed from the purifying and rectifying columns, are directly fed into a continuous bubble cap plate column (266). The overhead product of this

column contains most of the alcohol and some of the water present in the feed. A concentrated fusel oil stream is removed from the intermediate plates and passes to a decanter. The upper layer is decanted and forms the fusel oil by-product. The lower layer is returned to the lower plates of the column.

Subsequent purification of fusel oil for commercial use is generally achieved by means of either continuous or intermittent distillations. The purpose of this operation is to remove any ethyl alcohol and water remaining in the mixture, as well as the higher boiling fractions containing impurities of low volatility. Several processes of fractionation have been suggested in the literature.

Khshanouskii describes a fractional distillation method in which all fractions up to 97-98°C, which, according to him, contain all the lower boiling substances not allowed in fusel oil, have volatilized (292). The main distillation is then conducted to 135-7°C. The fraction remaining above this temperature is discarded.

Ullmann reports on a method in which the fusel oil to be purified is first de-watered with calcium chloride and subsequently fractionally distilled and separated into the desired fractions (320).

Longinov and Pryanishnikov have studied the fractionation of fusel oil in commercial scale without previous dehydration. Data is given on the amounts of propyl, isobutyl and amyl alcohols which pass over with the early fractions which contain the water and ethyl alcohol present in the original product (302).

A method has been patented in Germany in which mixtures containing

ethyl alcohol, water and fusel oil are fractionally distilled in the presence of an alkali or alkaline earth salt of an aliphatic acid, as, for example, a mixture of sodium acetate and potassium acetate (279). The salt may be added to the mixture in the still or the vapor from the still can be passed in counterflow with an alcohol solution or suspension of the salt. It is claimed that the process yields a 95% alcohol distillate and a residue of fusel oil.

The descriptions available in the literature on the above mentioned apparatus and processes consist of generalities. No specific values or operating conditions are given. Reflux ratios and proportions of substances added are not given in any case. Temperature range for the various fractions in fractional distillations are given in very few cases.

CHAPTER VI

AUTOMATIC CONTROLS IN THE ALCOHOLIC DISTILLATION

While planning the research work, which had as its objective the gathering of experimental data on fusel oil distribution in the rectifying column under different operating conditions, the need of utilizing an adequate system for controlling the operational variables was promptly recognized.

No information was found in the literature regarding the performance of automatic control systems used in the alcoholic distillation. In view of this lack of information and considering that the presence of continuously changing conditions would preclude the collection of reliable data, a series of experiments were conducted with the objective of establishing a control system which would fulfill the requirements of this particular distillation process. The results of these studies are presented in the following paragraphs.

To obtain satisfactory results in the operation of a distillation column, either continuous or intermittent, it is of utmost importance that the operating conditions be rigorously controlled. A continuous distillation unit, correctly designed and provided with an adequate control system is capable of producing overhead distillates, bottoms, and sidestream products of constant composition and, consequently, of uniform quality.

Once the column has attained equilibrium conditions and collection of the products has commenced, it is indispensable that such conditions of

equilibrium be maintained throughout the whole course of the operation. In numerous distillation processes, as in alcoholic beverages and industrial alcohol, the impurities to be eliminated during the distillation process are of such a nature that their presence in the final product, even in very small concentrations, greatly detracts from the quality of the latter. Unstable conditions in the column for relatively short periods of time may result in the presence of these impurities in the product receiving tank in sufficient concentrations to make necessary the reprocessing of the whole content of the tank.

Harbert has pointed out that, in most cases, lack of adequate control systems and not defective design, is responsible for deficient separations and deviations from theoretical expectations (335).

In the operation of a continuous distillation column the problem of control would be greatly simplified if it were possible to maintain constant the composition, the temperature and the rate of the feed stream. Under these conditions, and using automatic controllers to fix the other variables of the process--such as boil up rate; reflux rate; reflux temperature; pressure; rate of overhead, bottoms and side-stream products; and levels--the occurrance of variations and erratic conditions would be less frequent and serious. In industrial practice it is possible to maintain the temperature and the rate of the feed virtually constant. However, due to the characteristics and nature of commercial processes, it is impossible to maintain rigorously constant the composition of the feed. This gives origin to most of the variations and unstable conditions which develop during the operation of a continuous

column. Variations in the composition of the feed can be largely reduced, although not completely eliminated, by the use of fairly large intermediate receiving tanks between successive columns in the process.

The control system utilized should be capable of detecting deviations from steady conditions and of producing the required corrective action.

Numerous control systems have been suggested for the control of distillation columns. All have the common objective of maintaining the dynamic equilibrium of the column in such a fashion that a product of high and uniform quality is obtained.

In addition to the use of temperature as a function of composition, several other physical and chemical properties of product streams have been used as a basis for control systems. Among others, electrical conductivity, index of refraction and infrared radiations can be mentioned (348, 352, 357).

Numerous authors have studied the effect of controlling different operational variables in the performance of a distillation column.

Boyd has discussed in several publications the general principles governing the application of control systems to fractionating columns. The operation of control systems, based on maintaining a constant reference temperature in either the rectifying or the stripping section of the column, has been studied by this author (327, 328).

Hartmand and Braun have discussed the factors and principles affecting the use of controls from theoretical and practical points of view (336).

Uitti has studied the optimum location of temperature control

points and its effect on the operation of fractionation columns (354, 355).

The systems of control used in the operation of distillation columns can be classified as either "quantity control systems" or "composition control systems". In the former the rate of flow of the different streams to and from the column, as well as various levels, are maintained constant without any concern to varying compositions in the process. In "composition control systems" at least one variable is automatically or manually adjusted to maintain constant a reference temperature, or other property, at a given point which in turn will maintain a constant composition at that point and ultimately result in the production of overhead or bottom products of uniform composition. Bauer and Orr applied the McCabe-Thiele diagram to study analytically the use of "quantity control" and "composition control" systems to correct for variation in the composition of the feed to a column operating at high reflux ratios (326). These authors used as criteria of the adequacy of the control systems studied, the ability of the latter to maintain constant compositions in the top and bottom products of the column. As expected, they observed that control system based on "quantity control" are not capable of detecting and producing corrective actions against variations in the composition of the products and the liquid in the plates, produced by changes in the composition of the feed.

Most of the workers who have studied different methods of control for distillation columns have tackled the problem from the point of view of maintaining constant composition in one of the products from the ends of the column; i.e., the overhead distillate or the bottoms. Very little emphasis has been given to the ability of the various control systems to

maintain constant compositions at intermediate sections of the column from which side-streams would be withdrawn.

The operation of a modern continuous distillation unit for the production of industrial alcohol and beverages was described in Chapter V. The behavior of fusel oil in the purifying and rectifying columns was discussed. It was indicated that under conventional operating conditions the oil would be removed as a side stream from the rectifying column several plates above the feed plate. It was pointed out that the main product is also withdrawn as a side stream several plates below the top plate of the rectifying column. The operation of the beer and purifying columns of the unit is similar to the operation of the rectifying column with the exception that as mentioned above, two side-streams are removed from the rectifying column in addition to overhead and bottoms products. The withdrawal of side streams from two plates near the two extremes of the rectifying section, requires that the control system employed be capable of producing corrective actions without causing a shift in the distribution of compositions along the whole rectifying section. Constant compositions are required not only in the main product but in all plates of the rectifying section.

Considering that the control of the rectifying column is more complex than the control of the beer and purifying columns, from which only overhead and bottom products are removed, our work toward the development of an adequate control system for the alcoholic distillation was conducted with the rectifying column.

Once equilibrium compositions have been reached, it is indispensable

that these be maintained throughout the duration of the operation. Otherwise the location of the fusel oil accumulation band would be displaced along the column. Under equilibrium conditions the amount and composition of liquid and vapor in each plate remains constant. Consequently, the amount of alcohol hold-up in the system is constant. If the alcohol content in the feed decreases while the same amount of product is being removed, the composition of the latter would not re-adjust itself instantaneously in order to produce the required alcohol balance in the column. For a rather short period of time the composition of the main product in the upper part of the column will remain substantially uniform while the alcohol accumulated in the lower plates is depleted to such an extent that the composition of the product is affected. During this time-lag the temperature of the lower plates would increase steadily while the distribution of concentrations of fusel oil is displaced upward. If a corrective action is not produced soon enough by the automatic control system utilized, the displacement of the fusel oil band would produce an increase in the concentration of the latter in the upper trays of the column and consequently in the main product. The upward displacement of the fusel oil band would also produce a lower concentration of fusel oil in the plate where the maximum accumulation was formerly located and from where the side-stream is being removed. This in turn would offset the balance between the fusel oil entering and that leaving the column. Accordingly, the oil will continue to accumulate in the column until a concentration is reached at the plate from which the fusel oil side-stream is being removed that restores the oil balance. Again, this would result

in even higher concentrations of fusel oil in the upper trays and in the main product.

Should the alcohol content in the feed increase under similar operating conditions, the alcohol accumulation would then build up in the column to a point where the excess alcohol fed to the column would be lost in the bottom waste product.

It is evident that changes in the composition of the feed, irrespective of the direction in which they occur, should be promptly counteracted by corrective actions produced by the control system employed in the operation of the column.

The distillation unit of the Rum Pilot Plant of the Agricultural Experiment Station of the University of Puerto Rico is highly instrumented. The control system of each column includes automatic temperature controllers to regulate the temperature of the feed and the reflux streams at any desired value. The boil-up rate in each column is controlled by an automatic differential pressure controller which in turn resets an automatic steam flow rate controller to the reboiler. The differential pressure instrument is tapped near the bottom and top ends of the column. The rate of flow of the feed and the reflux streams are automatically controlled in all cases. The rate of flow of the finished main product in the rectifying column is also regulated by means of an automatic flow controller. The overhead product stream in each column and the fusel oil side-stream in the rectifying column are regulated by means of a precision calibrated rotameter. It should be recalled that the overhead product of the beer column constitutes the raw product of the process and that no

purification is intended at this column. The overhead products of the purifying and rectifying columns consist of "heads" streams which contain about 2% to 10% of the alcohol in their respective feeds. The flow of the bottom product of each column is regulated by an automatic level controller which maintains enough liquid in the column to cover the tubes of the reboiler. A 48 point push button temperature indicator and a 16 point strip chart temperature recorder, both of electronic measuring circuit and actuated by copper-constantan thermocouples, serves for indicating and recording temperatures at selected points of the process.

All flow rate and level controllers are of the pneumatic type. The flow rate controllers are provided with adjustable proportional band and automatic reset. These flow controllers can be reset by any other type of pneumatic controller working with output pressures from 3-15 psig. In the latter stages of our experimental work, a liquid-filled temperature controller was used to reset a flow rate controller to maintain constant a reference temperature at a selected point of the system.

In addition to the above listed instruments, precision calibrated rotameters are installed in series with the automatic flow controllers in the feed lines to the three columns and in the main product take-off. These rotameters are indicating instruments only and serve as a check to the calibration of the automatic flow rate controllers. All instruments, with the exception of the indicating rotameters, are installed on a graphic control panel in the second floor of the distillation tower. A photograph of the panel is included in the Appendix.

The following section describes a group of control systems which have been suggested in the literature for the operation of continuous

distillation columns. Quantity-Control System II and Composition Control System II and IIA were tried under actual operating conditions. Composition Control Systems III and IV represent modifications developed during the course of this work.

During the course of our studies no intentional variation on the composition of the feed was made. Hence, our work deals with the development of control systems capable of producing control actions to counteract changes which are inherent to the characteristics of the process. Periodic determinations of the alcohol content of the feed showed variations of 5% to 10% of the nominal feed composition.

In all cases operations were conducted at atmospheric pressures.

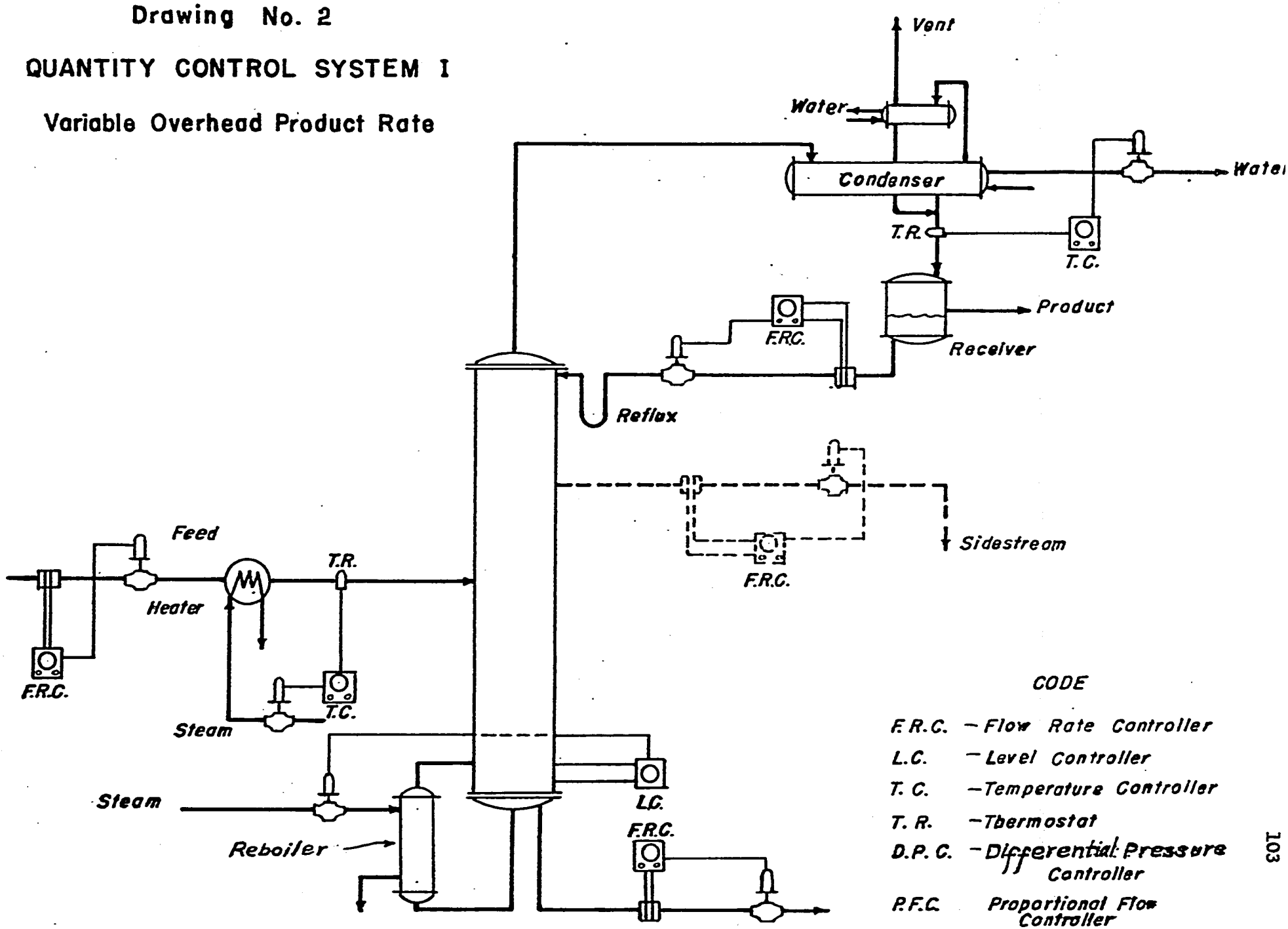
QUANTITY CONTROL SYSTEMS

Quantity Control System I: This system, patented by Nelson is a typical case of quantity control methods (343). The details of the system are shown in Drawing 2. The rate of flow and the temperature of the feed are maintained constant by means of automatic controls. The rate of the bottoms product is also maintained constant by means of an automatic flow rate controller. The boil-up rate is variable, being regulated by an automatic level controller which, in order to maintain constant the level of liquid in the bottom of the column, varies the rate of flow of steam entering the reboiler. The overhead distillate is condensed and passed into a receiver where it is divided into reflux and product streams. The temperature of the reflux in the patented process is maintained constant by manually controlling the amount of water entering the condenser. An automatic control actuated by a thermocouple installed in the reflux line,

Drawing No. 2

QUANTITY CONTROL SYSTEM I

Variable Overhead Product Rate



CODE

F.R.C. – Flow Rate Controller
L.C. – Level Controller
T. C. – Temperature Controller
T. R. – Thermostat
D.P. C. – Differential Pressure Controller
P.F.C. Proportional Flow Controller

as shown in Drawing 1, can be substituted for the manual operation. The reflux rate is maintained constant by means of an automatic flow rate controller. The product rate is variable. It leaves the condensate receiver through an overflow which, in turn, maintains constant the liquid level in the receiver.

The original drawing appearing with the patent does not show the removal of side-streams from intermediate plates. These could be withdrawn, if required, and their flow controlled by means of automatic flow rate controllers.

It is essential in the application of this control system that the composition of the feed be maintained rigorously constant. In the case of variations in the latter, which inevitably occur, this system would be incapable of detecting and correcting for these changes and, therefore, of producing a product of uniform quality and composition.

It could be used in those cases in which the bottom product of the column consists of a pure substance. To achieve this, the rates of flow of the feed and the bottoms product should be proportioned in such a fashion that the amount of the bottom product be less than the amount of that particular substance entering into the column with the feed stream. Obviously, it is assumed that the column have the number of trays required by the particular separation in consideration. In case of variations in the composition of the feed, the rate of flow of the bottom product should correspond to the minimum concentration possible in order to insure the purity of said product. Whenever the concentration of this substance in the feed is over the minimum, some of it will pass with the overhead distillate.

Keeping in mind the requirements for the control of the alcoholic distillation, we should conclude that this control system is not adequate for that particular process.

Quantity Control System II: This system, shown in Drawing 3, differs from System I in that the boil-up rate and the rate of flow of the overhead distillate are maintained constant while the rate of flow of the bottom product is variable. The latter is regulated by a level control while the overhead product is maintained constant by an automatic flow rate controller. The boil-up rate is automatically controlled by maintaining constant a differential pressure across the column, since the latter is a direct function of the former. A differential pressure controller resets the steam flow rate controller which regulates the entrance of steam into the reboiler. This procedure of controlling the boil-up rate is widely used in distillation processes.

Again, due to the absence of provisions for detecting and producing corrective actions to counterbalance alterations produced by changes in the composition of the feed, this system is not capable of giving products of constant composition and quality.

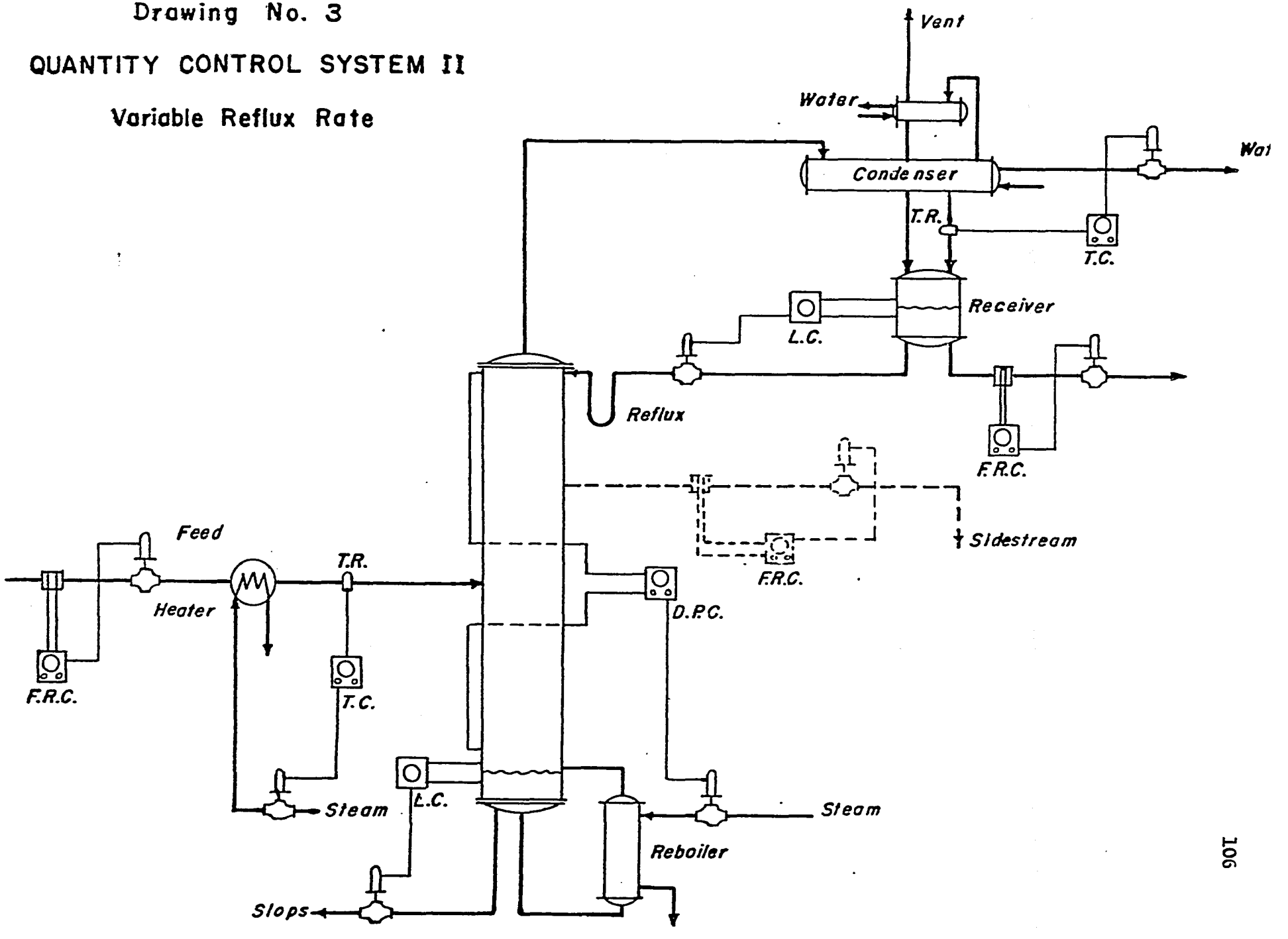
It could be employed in those cases in which an overhead product consisting of a pure substance is desired. This can be achieved by removing the overhead product at a rate equal to the minimum rate of feeding of this particular substance with the feed stream. Whenever the content of this substance in the feed is above the minimum composition, some of it will be present in the bottom stream of the column.

This system was used for the operation of our rectifying column

Drawing No. 3

QUANTITY CONTROL SYSTEM II

Variable Reflux Rate



in the course of our studies with the purpose of (1) determining the effectiveness of using rather large intermediate receiving tanks between columns to minimize variations in the composition of the feed, and (2) gathering experimental data which would indicate the effect of unsteady conditions in the distribution of alcohol and fusel oil along the column.

The control system applied was identical to that shown in Drawing 2 although the level controller shown in the distillate receiver was substituted with an overflow which produced identical results, i.e., maintaining a constant level in the condensate receiver.

Our rectifying column has 50 bubble cap trays, 15 inches nominal diameter at 12 inches between plates. Feed, consisting of the bottom product of the purifying column and containing about 30% alcohol by volume was added at plate 16. The main product was withdrawn from plate 42 as a side stream. Heads containing 2% of the alcohol fed were removed from the distillate collector. The boil-up rate was set to produce a reflux stream 5 times as large as the main product stream. The column was maintained at total reflux while feed was added continuously until a temperature was obtained in the plate above the feed plate corresponding to the composition of the feed. Upon entering the column, the feed mixes in the down-take with the liquid flowing from the immediate upper tray.

The experiment was run for seven hours after withdrawal of product commenced. Every hour samples were taken from plates 50, 46, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 22, 20, 18, 14, 12, 10, 8, and 6, counting from the bottom up. No fusel oil side stream was removed.

Tables II and III in the Appendix present, respectively, the alcohol

and fusel oil content in the various plates of the column at time intervals. Table II indicates a gradual exhaustion of the alcohol hold-up in the column. This will happen whenever the alcohol content in the feed falls below the value on which the material balance was based. Under these conditions more alcohol is removed in the product than is fed into the column. The data presented in Table III indicates a gradual displacement of the fusel oil concentration toward the upper plates of the column. The increase of fusel oil accumulation with time is due to the fact that no oil side-stream was removed.

The upward displacement of fusel oil is a direct consequence of the decrease in alcohol content of the plates. It can be noticed that in the first sampling period the maximum concentration of fusel oil is located at plate 26 where the apparent alcoholic strength is 129°P. At the end of seven hours the maximum concentration is at plate 34 where the apparent alcohol content is 131°P. At the beginning of the operation, the fusel oil content in plate 42, from which the main product was withdrawn, was 20 mg. per 100 ml. At the end of seven hours, due to the upward displacement of the fusel oil band, the fusel oil concentration on this plate reached a value of 460 mg. per 100 ml., yielding a product of very inferior quality. These results demonstrate the inability of the control system used to maintain uniform conditions through the course of the operation of the column.

As was mentioned in previous paragraphs, the feed to the rectifying column consists of the bottom product of the purifying column and its composition was not intentionally varied. The changes produced in such

compositions were inherent to the characteristics of the process.

Quantity Control System III: In this system, shown in Drawing 4, the temperature and the rate of feed, as well as the temperature of the reflux stream and the liquid level in the bottom of the column, are again maintained constant by means of automatic controllers. The boil-up rate is controlled in a manner identical to that described for Quantity Control System II, based on a constant differential pressure across the column. The rate of flow of the bottom product is variable being regulated by the level controller installed in the bottom of the column. In this system, the ratio between the reflux and overhead product streams is maintained constant by means of a ratio-controller actuated by the liquid level in the reflux collector.

By maintaining a constant reflux ratio it is intended to prevent drastic reductions in the rectifying capacity of the column which could be produced by individually readjusting either the reflux or the overhead product streams in order to correct erratic conditions in the process.

As with all quantity control methods, this system may be employed when the feed can be maintained substantially constant and when the rate of flow of the various streams are proportioned to insure the production of a pure substance as one of the products. If all the products from the column consist of solutions of two or more substances there is no way of maintaining constant compositions in the end products when variations in the composition of the feed occur.

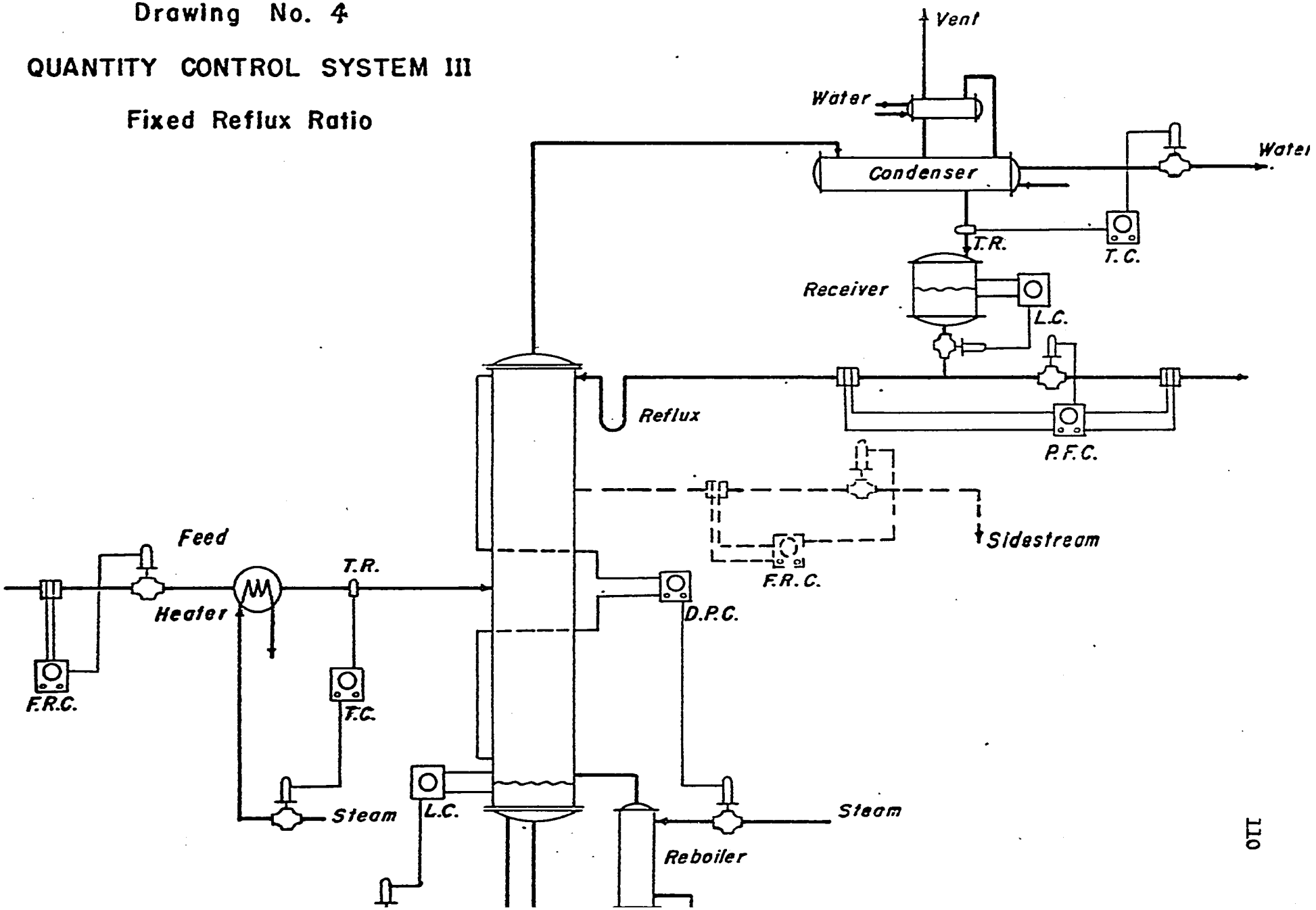
COMPOSITION CONTROL SYSTEMS

When it is desired to obtain products of constant composition,

Drawing No. 4

QUANTITY CONTROL SYSTEM III

Fixed Reflux Ratio



either from the ends or from intermediate plates of the column, it is necessary to resort to the principle of composition control. This type of control system, as applied to distillation processes, involves the detection of unsteady conditions as reflected by changes in temperature and the production of the necessary corrective action to maintain constant one or more reference temperatures. The corrective action usually consists of altering the rate of flow of a given stream or streams or of readjusting the boil-up rate.

Composition Control System I: This system, shown in Drawing 5, differs from Quantity Control System III, discussed above, in that a temperature controller is used to regulate the boil-up rate of the column in order to maintain constant a reference temperature at a given point of the column. The point at which the reference temperature should be maintained constant can be located anywhere along the column depending on the particular process under consideration. For the selection of this point several factors should be considered including (1) time lags, (2) coefficient of temperature change with changes in composition, and (3) region of the column where constancy in composition is required.

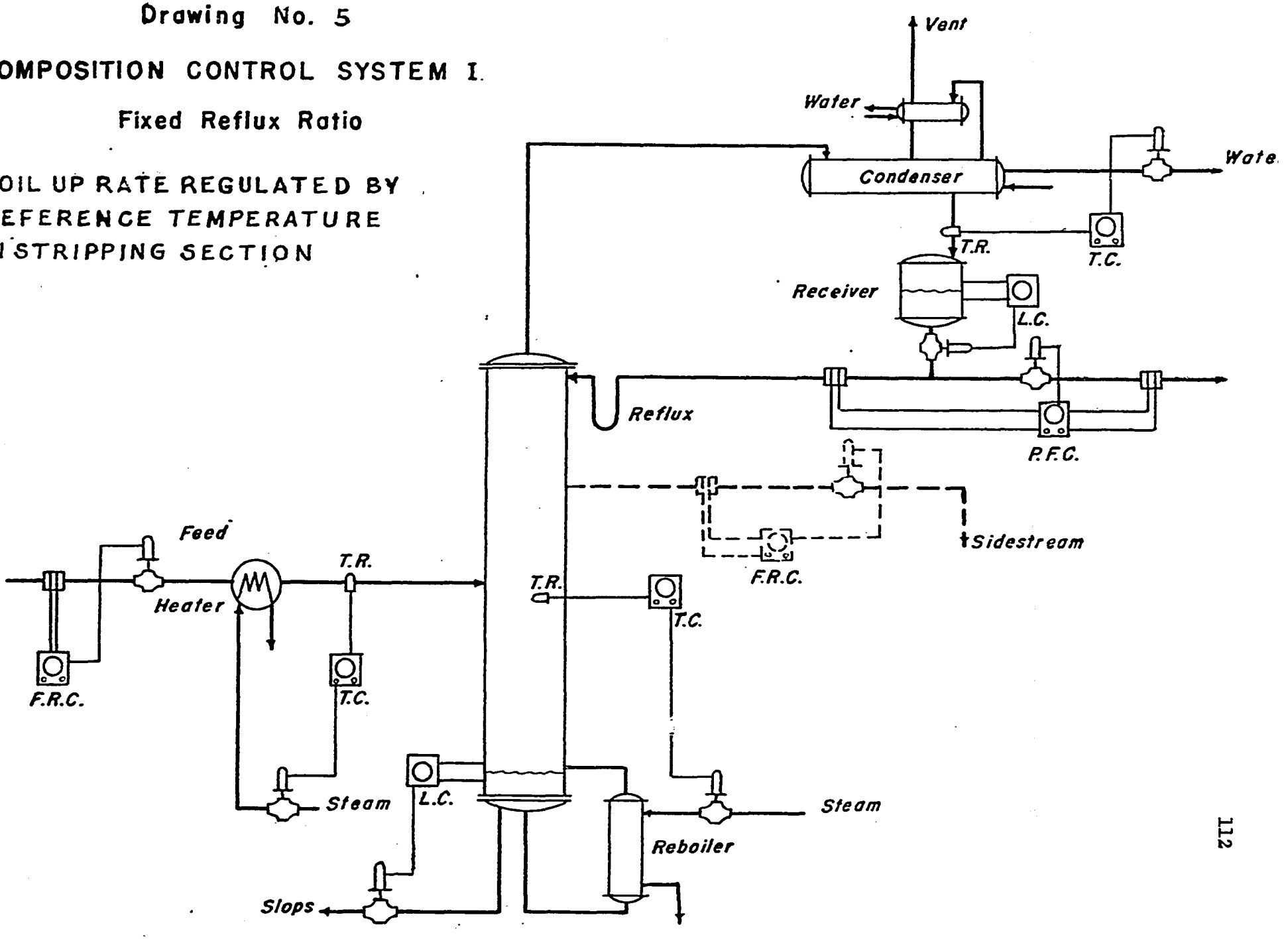
This particular system gives satisfactory results specifically when the composition of one of the ends products of the column is desired constant. The fact that the boil-up rate and the reflux rate are varied, offers the danger of flooding the upper trays of the column, should drastic corrections be effected. Erratic conditions which would require a drastic reduction of the boil-up rate may result in a sudden decrease in the rate of flow of the reflux stream with the possibility of not having enough

Drawing No. 5

COMPOSITION CONTROL SYSTEM I.

Fixed Reflux Ratio

BOIL UP RATE REGULATED BY REFERENCE TEMPERATURE IN STRIPPING SECTION



liquid flowing down the column after a relatively large side-stream is removed in any given process such as the alcoholic distillation. One additional disadvantage of control systems based on varying the boil-up rate to produce the required corrective action, is the fact that changes in the amount of evaporation cause corresponding changes in the pressure prevailing inside the column. This effect, which is greater in the lower plates of the column, produces subsequent readjustments in the vapor and liquid compositions by plates when the reference control temperature is maintained constant.

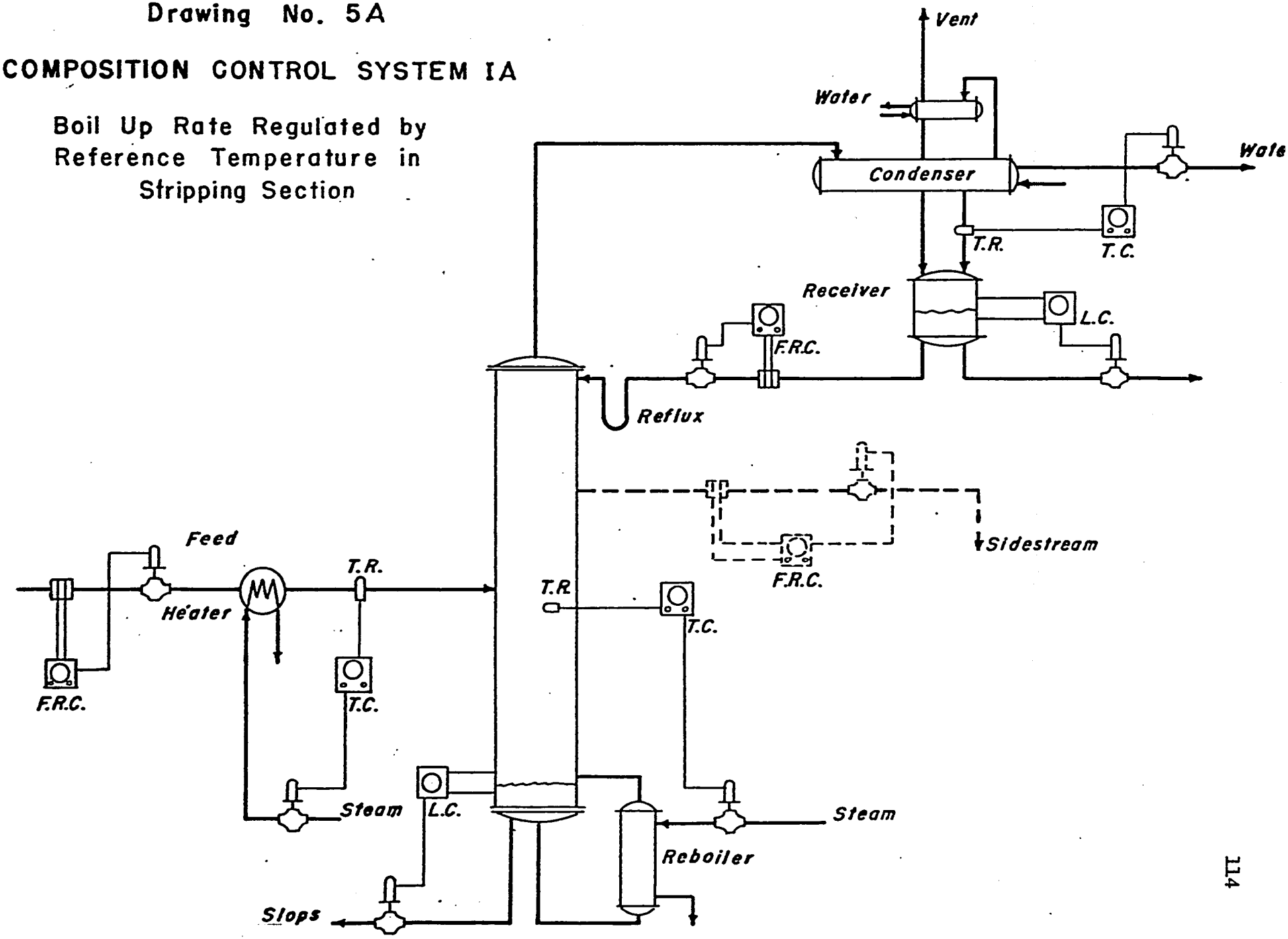
A modification to this system is presented in Drawing 5-A as Composition Control System I-A. The only difference consists of replacing the automatic ratio controller, which in the former system maintained a constant reflux ratio, with a simple flow rate controller which maintains constant the rate of reflux to the column while the amount of overhead distillate is variable. The latter is regulated by a level controller which maintains a constant liquid level in the reflux collector.

Composition Control System II: This system, shown in Drawing 6, is extensively used for the control of continuous distillation columns (329, 338). As in the previously described systems, the temperature and the rate of feed, as well as the temperature of the reflux stream are maintained constant by means of automatic controllers. The rate of flow of the bottom product is again regulated by a level controller that maintains a constant liquid level in the bottom of the column. The boil up rate is controlled by a set differential pressure across the column. Intermediate

Drawing No. 5A

COMPOSITION CONTROL SYSTEM IA

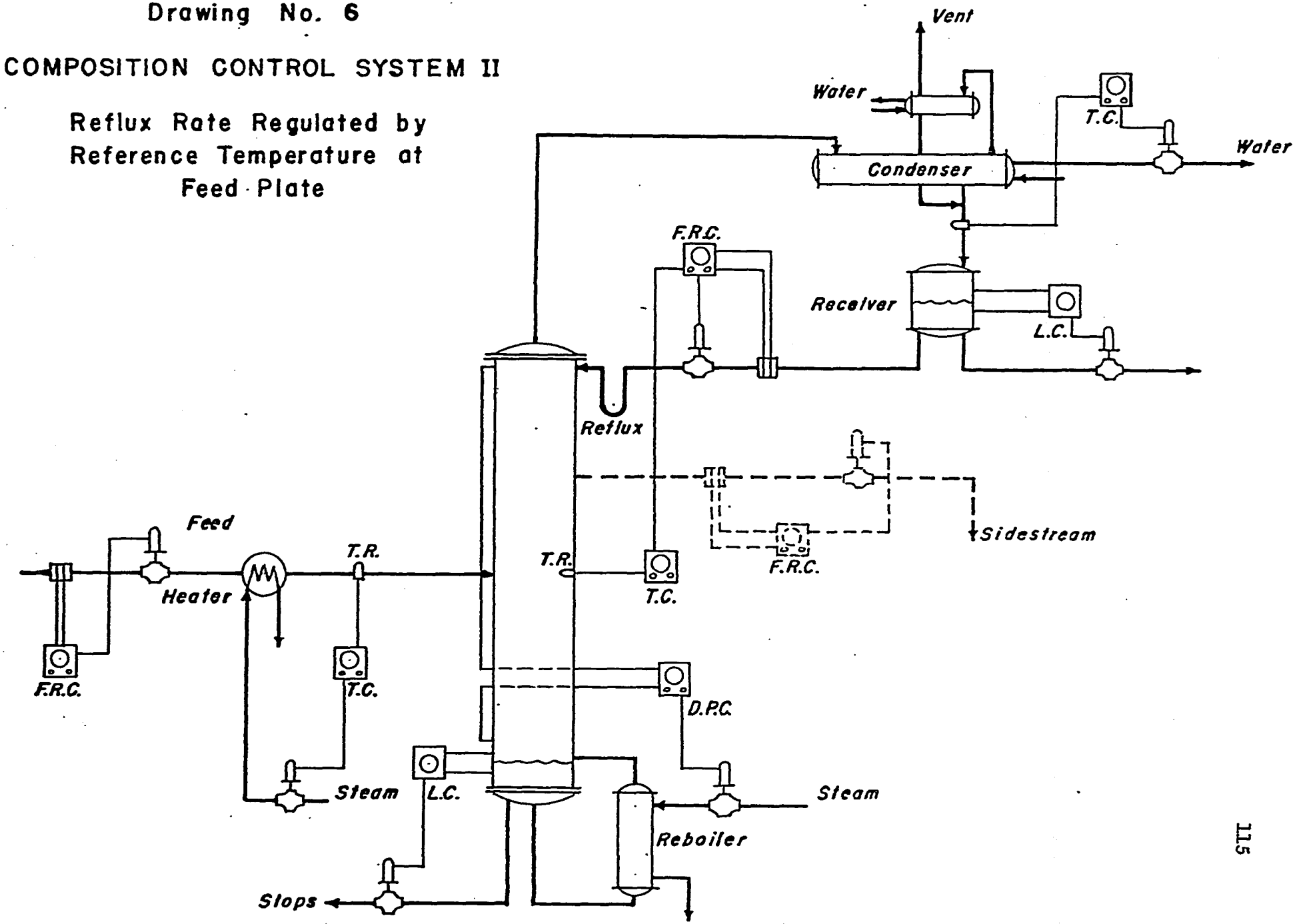
Boil Up Rate Regulated by Reference Temperature in Stripping Section



Drawing No. 6

COMPOSITION CONTROL SYSTEM II

Reflux Rate Regulated by Reference Temperature at Feed Plate



side-streams, if present, are maintained constant by means of automatic or manual flow rate controllers. The rate of flow of the reflux stream is regulated by a temperature controller whose sensitive element installed in an intermediate point in the column. The flow of the overhead distillate is regulated by a level controller installed in the reflux collector.

A modification of this system, presented in Drawing 6-A as Composition Control System II-A, consists of regulating the amount of overhead product by means of the temperature controller while the rate of reflux to the column is regulated by the level controller that maintains a constant liquid level in the reflux collector.

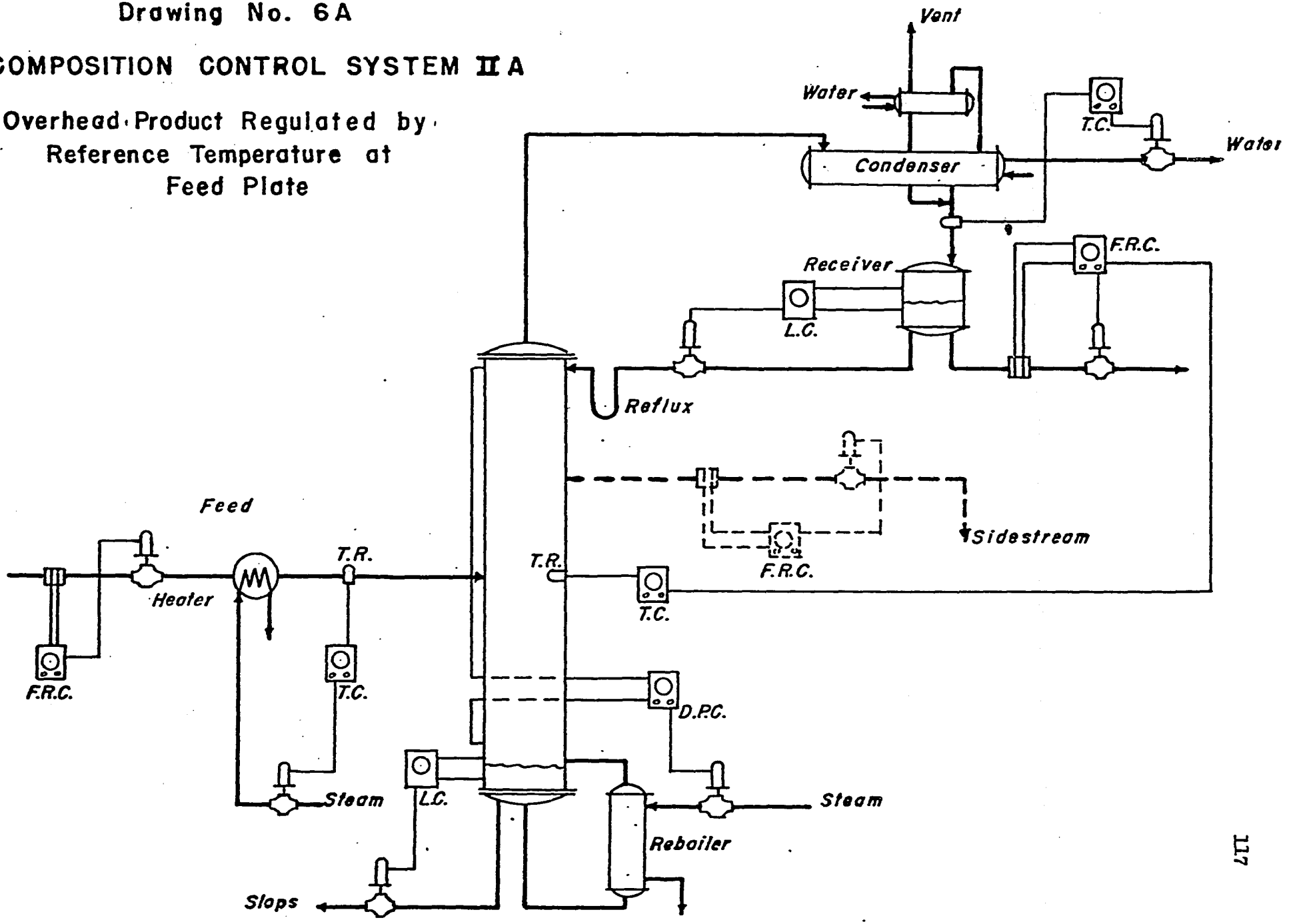
The two described alternatives of this type of control system were used in special runs in which the main product was obtained as the overhead distillate of the column instead of removing it as a side stream which constitutes the conventional practice in modern continuous distillation units.

The location of the temperature reference point was the subject of careful studies and preliminary runs. It has been previously mentioned that this point should fall in a region where rather large changes in temperature are obtained with a given change of composition. Further, when alterations to steady conditions occur, they should be detected and the corresponding corrective action brought about before changes in composition are produced in the top of the column from which the main product is obtained in this particular process. It has also been pointed out that in the alcohol distillation it is necessary that constant compositions be maintained across the whole rectifying section of the column since a fusel

Drawing No. 6A

COMPOSITION CONTROL SYSTEM II A

Overhead Product Regulated by Reference Temperature at Feed Plate



oil side-stream is withdrawn from plates over the feed plate. Having these factors in mind, it was decided that the reference temperature on which the control system would be based, would be that of the vapor space of the plate immediately over the feed plate. By selecting the right temperature value, the liquid of that plate, which mixes with the feed in the downtake, would have the same composition as the feed itself. The importance of introducing the feed on the plate where the liquid has a composition as similar as possible to that of the feed has been pointed out by authors on the subject (330, 351). There are definite limits for the location of the feed plate in order to get an operable design. Beyond these limits an infinite number of plates would be required for the desired separation.

For our experiments, high quality 190°P alcohol was diluted with water to a binary mixture of 30% alcohol. This mixture was processed through the purifying column and the bottom product collected in an intermediate receiving tank from where it was fed into plate 16 of the rectifying column. A reflux ratio of 5:1 was utilized in the latter. The experiments were run for five hours after withdrawal of product commenced. Samples and temperature readings were taken every hour from plates 50, 42, 36, 30, 24, 20, 18, 14, 10, and 6. The samples were analyzed for alcohol content. Manual control was utilized to maintain constant the reference temperature in the column.

Table IV and V in the Appendix, present, respectively, the alcohol content and the temperature by plates when using the control system based on varying the rate of the reflux stream to maintain constant the reference

temperature in the column. Tables VI and VII present similar data for the run in which the control system based on varying the distillate stream was utilized.

The data obtained indicate that very satisfactory results are obtained when utilizing the control system based on varying the distillate stream. Although a high value was selected as reference temperature while trying to account for the pressure prevailing in the column, thus producing rather low alcoholic contents in the feed plate, the results serve very well the purpose of indicating that this control system can maintain uniform compositions in the rectifying section of the column.

Greater variations were observed when the method of altering the reflux rate to control the operation was used. These are specifically noted in the intermediate plates of the column where changes in feed composition are first reflected. Very good uniformity was obtained, however, in the upper trays of the column and in the top product.

Since the size of the overhead product stream is normally several times smaller than the reflux stream, less drastic variations occur in the operating variables of the column when making proportional adjustments to correct tor deviations while using System II-A.

Composition Control System III: The results obtained with composition Control System II-A were very satisfactory. In the alcoholic distillation, however, the overhead distillate is not the main product. In turn, it constitutes the "heads" stream which is very small, being usually from 100 to 300 times smaller than the reflux stream. It is evident that a control system based on altering such a small stream would be inadequate.

With the objective of satisfying the requirements of the alcohol distillation process a modification was developed which is presented in Drawing 7 as Composition Control System III. In this system the reference temperature is maintained constant by varying the rate of flow of the main product which is removed as a side stream several plates below the top plate of the column. The rate of the reflux stream is maintained constant by means of an automatic flow rate controller. Similarly, the rate of "heads" take-off is maintained constant. This operation requires that the differential pressure across the column--which regulates the rate of evaporation in the column--be set at a specific control point which would produce a boil-up rate equal to the rate of reflux plus the rate of "heads" take-off. This set point can be easily established in practice. It is our experience that, although apparently rigid, this control system works very well in actual practice. The objection to this apparent rigidity could be eliminated by installing an automatic liquid level controller in the reflux collector which, in turn, would reset the control point of the differential pressure controller.

For controlling the rate of flow of the fusel oil streams as well as the "heads" stream, variable area rotameters provided with needle valves for manual control, have been used with great success.

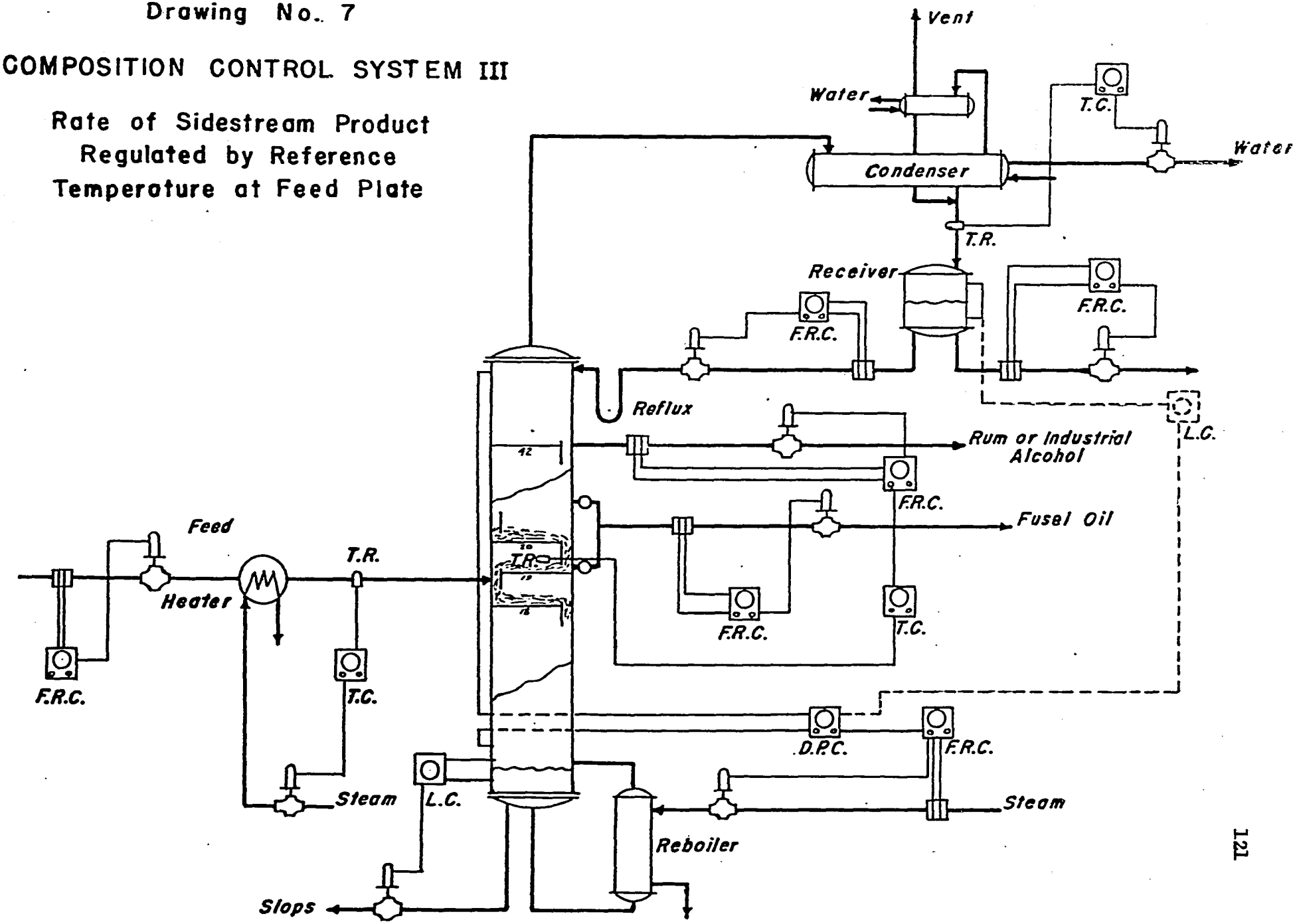
Composition Control System III was tested in experimental runs and later used with great success in the routine operation of the plant until Composition Control System IV, to be discussed in later paragraphs, was developed.

Table VIII and IX present, respectively, the apparent alcoholic

Drawing No. 7

COMPOSITION CONTROL SYSTEM III

Rate of Sidestream Product
Regulated by Reference
Temperature at Feed Plate



strength and the fusel oil content by plates of the column for one experiment while Tables X and XI give similar data for a second experiment. In both cases a feed consisting of the bottom product of the purifying column and containing about 30% alcohol by volume was introduced at plate 16 of the column; a reflux ratio of 5:1 was used; the main product was withdrawn from plate 42, and about 3% of the alcohol fed to the column was removed in the "heads" stream. Samples were withdrawn from numerous plates at various time intervals as shown in the tables of results. The first experiment was run for 12 hours after withdrawal of main product commenced while the second was run for 24 hours. No fusel oil side-stream was removed in either case during the operation with the purpose of studying the effect of continuously increasing accumulations of fusel oil in the plates of the column.

Very good uniformity was obtained in the distribution of apparent alcohol content through the column especially in the rectifying section. The increase noticed in the plates neighboring the feed plate is due to the continuously increasing concentration of fusel oil around these plates. These deviations, however, are not reflected in the alcoholic content of the upper 25 plates of the column producing a very uniform main product.

The accumulation of fusel oil in the column increases continuously during the course of the operation since, as mentioned above, no oil side stream was removed. The data indicates that there is no displacement of the band of fusel oil concentration during the whole duration of the run. It was centered around plate 19 in both experiments. The results of a series of experiments specifically designed for gathering data on fusel

oil distribution along the column are discussed in the next chapter.

Composition Control System IV: The methods of control based on maintaining constant a reference temperature by varying either the reflux or product streams are capable of producing satisfactory results, especially when uniform compositions are desired in the products from either end of the column.

In previous paragraphs, it has been indicated that changes in the composition of the feed constitute the most common source of variations in the equilibrium conditions of the column. Consequently alterations will first occur in the region neighboring the feed plate. As mentioned before, the corrective action usually consists of varying the size of either the reflux or the main product stream or even altering the boil up rate. Necessarily, the effect of this corrective action would be reflected across a section of the column since by this procedure, we are trying to correct an unbalance originating in a point of the column by altering the operating conditions at a second point physically apart from the first. While the necessary adjustments are effected to return the feed plate to the desired equilibrium conditions, a sequence of small alterations would occur in the intermediate plates which, in turn, may produce momentary displacements of substances accumulated on those plates from which side-streams are normally removed.

Should rather large fluctuations occur in the composition of the feed, these would be reflected in the quality or in the quantity of main product produced. Assuming that Composition Control System III is being utilized--which so far has been shown to better satisfy the requirements

of the alcohol distilling process--and that the alcohol content in the feed increases significantly, the automatic control instruments would tend to increase the size of the main product stream to remove the additional alcohol entering the column. In so doing, the internal reflux ratio of the column, from the main product take-off plate down, would be reduced since the boil-up rate remains constant. This change in the reflux to vapor ratio would obviously produce changes in the distribution of fusel oil by plates which could result in a product rich in fusel oil. In the next chapter it will be shown that the fusel oil band is displaced upward with lower reflux ratios. In the situation just described, the automatic control system would probably not cause great variations in the alcohol distribution in the rectifying section of the column since its action has been that of selecting a lower reflux ratio to handle a richer feed in alcohol while the reference temperature is maintained constant just above the feed tray. The data presented in the next chapter shows, however, that the distribution of fusel oil and the amplitude of the concentration band depends largely on the reflux ratio utilized. Much greater concentrations of fusel oil would be found at a plate whose liquid contains 185°P when a reflux ratio of 3:1 is utilized than would be found in a plate whose liquid is also 185°P but when a reflux ratio of 5:1 is used. Further, it has been found experimentally that below certain reflux ratios there is no sharp accumulation of fusel oil which results in relatively large concentrations of the oil in the upper section of the column.

On the other hand, if the alcohol content in the feed becomes lower, the control system would reduce the size of the main product stream, which would, in turn, reduce the productive capacity of the column, besides

producing alterations in the distribution of concentrations along the column. Should it be desired to restore the normal production capacity of the column, it would be required then to vary another group of variables such as the feed rate and the boil up rate with consequent alterations in the equilibrium conditions of the system.

It is not probable that extremely large changes would occur in the composition of the feed, especially if intermediate receiving tanks of adequate capacity are used between columns. In the case in which feed, normally at 40% alcohol by volume is added to the column, a decrease to, say, 38% alcohol, would be handled readily by the control system without causing any noticeable shift in the distribution of fusel oil. This, however, would represent a 5% decrease in the productive capacity of the plant, which would not be desirable.

In none of the control systems described in the literature and suggested for the operation of continuous distillation columns is it recommended that the feed stream be varied as a corrective action for alterations in the equilibrium conditions of the system. It has been repeatedly mentioned, however, that in the alcoholic distillation, due to the presence of side-streams, it is required that the compositions in the whole rectifying section of the column, and not just in the upper trays, be maintained constant to insure uniformity in the quality of the products removed. With this concept in mind, let us revise the equation of the "operating line" which governs the distribution of compositions in the rectifying section for the separation of a binary mixture. This equation is given by:

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_d$$

where:

y_n = Composition of the vapors leaving plate n; mol fraction

L_{n+1} = Moles of liquid flowing from plate n+1

V_n = Moles of vapor leaving plate n

x_{n+1} = Composition of liquid flowing from plate n+1; mol fraction

D = Moles of distillate

x = Composition of distillate; mol fraction

From this expression, it can be seen that any control system based on altering the variables involved in the equation would produce changes in the compositions of the rectifying section. The control methods described so far involve the variation of either L, D or V. When side-streams are present other operating lines are introduced whose equations are of similar form and involve the corresponding values of the same variables for the section under consideration.

It can be concluded that if the operational variables are maintained constant, the compositions of the liquid and the vapor in the different trys of the rectifying section would be constant as long as the composition of the vapor entering said rectifying section from the feed plate is constant. It can be seen that the size and the composition of the feed stream does not appear in the above given equation.

The equation for the stripping section operating line is given by:

$$y_m = \frac{L_{m+1}}{V_m} x_{m+1} - \frac{W}{V_m} x_w$$

If the feed is introduced at its boiling point and assuming equimolar latent heat of vaporization for the substances present, we find that:

$$L_{m+1} = L_n + F$$

where:

L_{m+1} = Liquid flowing down the stripping section; mols

L_n = Liquid flowing from the rectifying section; mols

F = Feed, mols

Besides:

$$W = F - (D + S_1 + S_2 + \ldots\ldots S_n)$$

where:

W = Bottom product; mols

D = Distillate; mols

S_1, S_2, S_n = Side-streams; mols

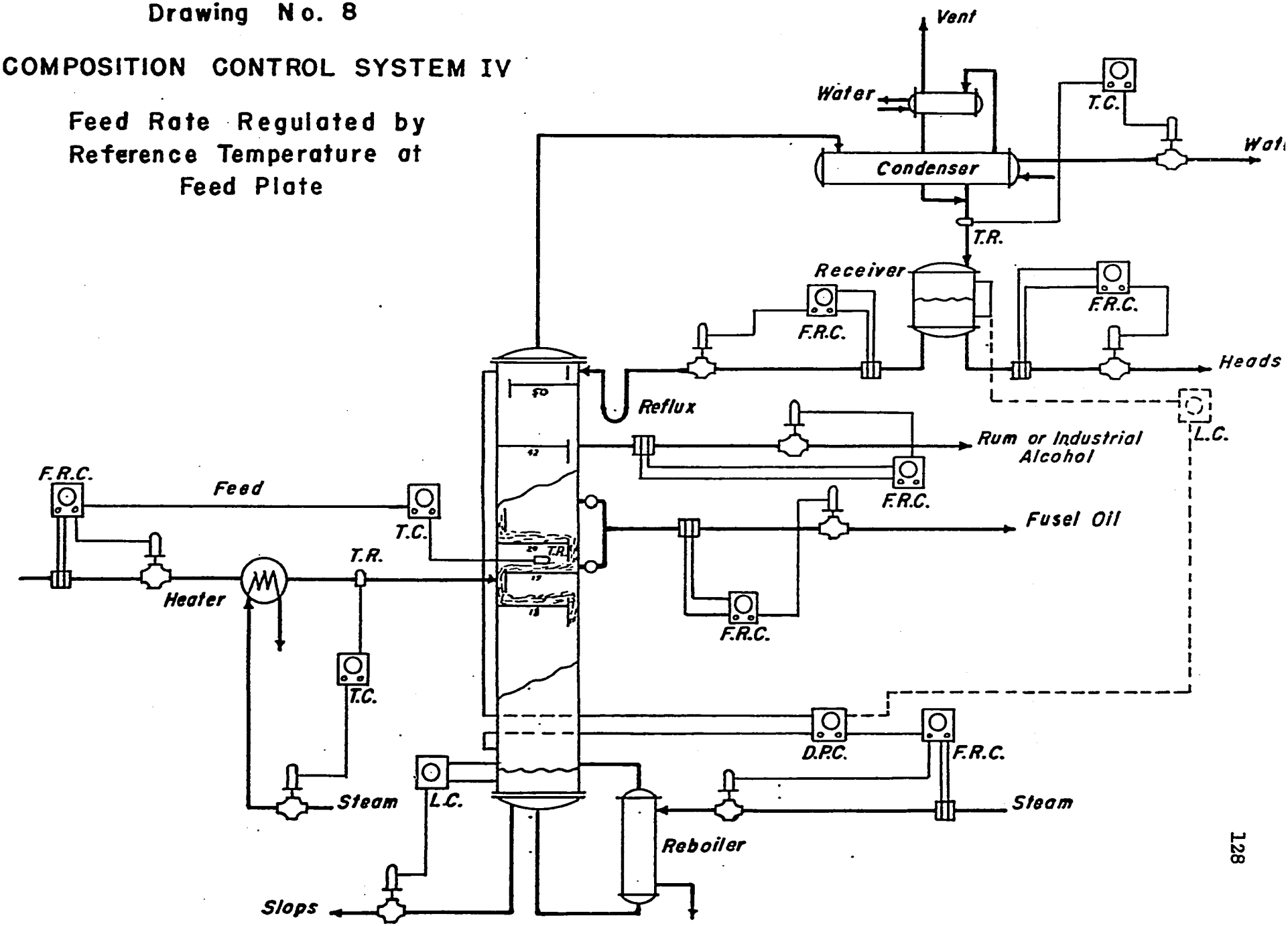
Accordingly, changes in the rate of feed to compensate for changes in its composition, would produce variations in the compositions at the different plates of the stripping section of the column. It has been indicated that in the alcoholic distillation no side-streams are removed from this section. Further, the bottom product of the latter consists of water and dissolved impurities being discarded. The only requirement is the prevention of alcohol losses in the bottom wastes. This can be achieved by specifying enough plates in this section to handle the extreme conditions expected.

In line with this reasoning, Composition Control System IV, presented in Drawing 8, was developed and tested under actual operating conditions. This system differs from Composition Control System III, in

Drawing No. 8

COMPOSITION CONTROL SYSTEM IV

Feed Rate Regulated by Reference Temperature at Feed Plate



that the automatic temperature controller varies the rate of feed to the column in order to maintain constant the reference temperature in the plate above the feed plate. The rate of flow of the main product side stream is maintained constant by means of an automatic flow rate controller. By this procedure all variables entering in the equation of the "operating line" of the rectifying section are maintained constant.

Essentially, by varying the rate of feed to produce the required corrective action, we are maintaining constant the input of alcohol into the column instead of the feed input. Further, since in many cases it is likely that even when variations in the alcohol content of the feed occurs, the ratio of fusel oil to alcohol may be approximately constant, the use of this control system results in maintaining a constant input of fusel oil into the column which would add to the stability of fusel oil accumulation in the column after steady state conditions have been attained.

When variations in the composition of the feed occur, the composition of the liquid in the feed plate would also vary producing corresponding variations in the vapor leaving this plate and entering the rectifying section of the column. This will produce subsequent variations in the compositions of the plate immediately above the feed plate which in turn will be reflected in its temperature. Upon detecting this temperature variation, the automatic temperature controller will alter the rate of feed as required to return the reference temperature to its set value and consequently restore equilibrium conditions in the rectifying section of the column.

Suppose that while operating under equilibrium conditions the

alcohol content in the feed suddenly decreases. This will produce a decrease in the alcohol content of the feed plate which in turn will produce subsequent alterations which will be reflected in the reference temperature on which the control system is centered. The automatic temperature controller will reset the feed flow rate controller to increase the amount of feed entering the column. By augmenting the rate of feed, the interior reflux ratio of the stripping section, given by L_{m+1}/V_m, is also increased. From the "operating line" equation for the stripping section it can be seen that a greater value of L_{m+1}/V_m represents an increase in the enriching capacity of the plates of that section. The control system will vary the rate of feed until such a value of L_{m+1}/V_m is obtained that compensates for the lower alcoholic composition now present in the feed plate region and the composition of the vapors entering the rectifying section is restored to the steady state conditions. This in turn will bring the reference temperature to its set value.

In the case of an increase in the alcohol content of the feed, the corrective action produced would be the inverse of that just described.

It can be observed that this control system possesses the distinct advantage of detecting changes at the point where they generally originate and proceed to correct them locally without producing a series of subsequent alterations along the rectifying section of the column. Time lags are substantially reduced.

Tables XII and XIII, in the Appendix, present, respectively, the alcohol content and the distribution of fusel oil concentration at several time intervals during 24 hours. In this experiment 80° Proof alcohol was

introduced at plate 18. A reflux ratio of 4:1 was utilized. The feed consisted of the bottom product of the purifying column. About 3% of the alcohol entering with the feed was removed as a head stream in the rectifying column. The main product was removed from plate 42 as a side stream. Tables XIV and XV present similar data for a second experiment conducted under similar conditions with the exception that a 3:1 reflux ratio was utilized. In both cases removal of the fusel oil side-stream was commenced after twelve hours of operation. The nine hour samples were analyzed to determine the plate of peak concentration. The accumulation of fusel oil in the column increased steadily during this period. Since there is no instantaneous method of analysis which will indicate the concentration of fusel oil in the plate of peak accumulation at the precise moment in which withdrawal of this product is to be started, a rate of 0.5 gallons per hour was selected for this stream. When removal of this side-stream is commenced, there would be adjustments in the accumulations of fusel oil until a balance is established between the oil entering and that leaving the column. If the oil take-off stream is too small the concentrations will continue to increase. On the other hand, if the stream is too large, the concentrations of fusel oil in the plates will decrease until the necessary balance is established. Variations in the fusel oil content of raw distillate from different fermenters will produce similar adjustments. Manual control was used in these experiments to vary the rate of feed in order to maintain constant the set reference temperature.

From the data obtained, it can be observed that the location of the peak concentration remains on the same plate during the whole operation.

Apart from small variations in the region adjacent to the feed plate, where relatively high concentrations of fusel oil are obtained, excellent stability in alcohol content by plates of the rectifying section prevailed at all times. The same applies to the distribution of fusel oil. The uniformity of the compositions of the upper 25 plates at all times is striking.

The results obtained with this control system in these experiments and in subsequent operations of the Rum Pilot Plant were so satisfactory that it was adopted as the standard control system for all research work as well as for routine operations. A liquid-filled automatic temperature controller has been installed which automatically resets the feed flow controller. The system was used for the experimental work on fusel oil distribution presented in the next chapter and in all operations of the Rum Pilot Plant. Its use was extended to the purifying column. In the beer column no purification is effected and the only precautions required is the prevention of alcohol losses in the bottom slops. Usually, this column is operated by setting the maximum rate of feed allowed by the feed controller and by varying the rate of distillate take-off to maintain constant a reference temperature below the feed plate.

Level controllers have been installed in the reflux collectors of the purifying and rectifying column which can be used to reset the differential pressure controllers in order to maintain constant boil-up rates. After more than two years utilizing Composition Control System IV, it has been found that the required variations in feed rate do not produce any noticeable increase in the pressure drop across the column for a given boil-up rate.

The use of this control system is by no means limited to the continuous alcoholic distillation. It could be used advantageously in any process requiring the removal from the rectifying section of intermediate side-streams of uniform composition. Its use facilitates the control of the operation and at the same time results in more uniform productive capacity and product quality. Intermediate receiving tanks between columns are required for its application. In the production of alcoholic beverages and industrial alcohol, it is sometimes found that the product of one column, either in the liquid or the vapor phase, is fed directly to a subsequent column. In that particular case, Composition Control System IV is not applicable. The use of Composition Control System III is recommended.

CHAPTER VII

EXPERIMENTAL DATA ON FUSEL OIL DISTRIBUTION IN THE RECTIFYING COLUMN UNDER DIFFERENT OPERATIONG CONDITIONS

The possible application of fusel oil distribution data in the design and operation of alcohol distillation units was discussed in Chapter V. It was pointed out that there is a virtual absence of this kind of data in the literature. Uncertainties regarding the nature and relative concentrations of the various constituents of fusel oil in any particular case preclude the application of theoretical methods for its prediction. In order to fill this need, a series of experiments were conducted under different operating conditions. The results of this work are presented in the following paragraphs.

The effect of utilizing different reflux ratios and alcoholic contents in the feed was studied. Feed compositions of 20, 30, 40 and 50 per cent alcohol by volume at 60°F were used. These values cover the range of compositions usually found in commercial practice. Each feed composition was studied under reflux ratios of 5:1, 4:1, 3:1 and 2:1, expressed as the ratio between the volumetric rate of flow of the reflux and the main product streams. These reflux ratios cover the range usually utilized in commercial practice. The minimum reflux ratio required to concentrate a 40% alcohol feed into a 95% alcohol product is 0.93.

Since the main product is withdrawn as a side-stream, the ratio between the amount of liquid flowing down the column from the product take-off plate and the amount of main product being withdrawn becomes one unit less than the nominal reflux ratio based on the external reflux

stream added to the top of the column. Accordingly, when the ratio between the external reflux stream and the main product stream is 5:1, the ratio between the internal reflux from the product plate down and the main product stream is correspondingly 4:1.

In addition to the above mentioned experiments, reflux ratios of 15:1 and 10:1 were utilized with a 30% alcohol feed. In two other experiments, feeds of 60% alcohol were distilled at reflux ratios of 5:1 and 2:1. In order to study the effect of fusel oil content in the feed on the location of the fusel oil band in the column, two additional experiments were run at a 3:1 reflux ratio and 40% alcohol in the feed. In one case, the feed was prepared by diluting high class spirits to the desired proof while adding calculated amounts of concentrated fusel oil to produce an oil concentration approximately one-half of that obtained in the 40% alcohol feed. In another case, the regular raw product from the beer column was diluted to 40% alcohol while adding enough fusel oil to produce an oil concentration approximately twice as large as that found normally. The results of these two additional experiments were compared with that in which regular 40% alcohol feed was distilled utilizing a 3:1 reflux ratio.

The operational procedure utilized in all experiments was as follows. Fermented molasses mash was fed into the beer column at a rate of about 100 gallons per hour. The exhausting section of this column contains 25 sieve plates, 12 inches nominal diameter at a plate spacing of 18 inches. The rectifying section consists of 4 bubble cap plates also at a spacing of 18 inches. An impingement plate separates the two sections with the

purpose of preventing solids from entering the top of the column. A reflux ratio of about 2:1 was utilized in all cases. The overhead product stream was adjusted to yield a product of about 60% alcohol by volume at 60°F. The raw distillate was collected in 500 gallon receiving tanks and diluted to the desired alcoholic strength. This mixture was subsequently fed into plate 16 of the purifying column, described in Chapter V. This column, as mentioned before, contains 40 bubble cap plates, 8 inches nominal diameter at 10 inch plate spacing. The rate of feed to the purifying column was established according to the nominal rate of feed to the rectifying column required in each particular experiment. A 190°P "heads" stream was removed in all cases from the overhead distillate of the purifying column. The size of this stream was such that it contained about 3% of the alcohol entering with the feed. A reflux ratio of 25:1 was utilized in all cases. The bottom product from the purifying column was collected in a 500 gallon receiving tank from where it was fed into plate 18 of the rectifying column. The operation was timed in such a fashion that this receiving tank always ran about half full. As mentioned in Chapter V, the rectifying column contains 50 bubble cap plates, 15 inches nominal diameter at a 12" plate spacing.

In the starting of operations of all columns, the bottom product discharge valve was closed and enough hot water charged into the column to cover the tubes of the reboiler. Steam was admitted to the reboiler and evaporation started. Water at its boiling point was intermittently added to maintain a constant level in the reboiler. When a certain boil-up rate was obtained the bottom product discharge valve was set to work

automatically and the continuous addition of the alcohol feed started under total reflux conditions. Addition of feed under total reflux was continued until a desired reference temperature was obtained at a given point of the column. Meanwhile, the control point of the differential pressure controller was adjusted to produce the boil-up rate required in each particular case. Withdrawal of products was then started.

For the operation of the rectifying column, a preliminary run was made the day previous to each experiment to determine under actual operating conditions the temperature value which should be used to produce a liquid composition in the plate just above the feed plate, approximately equal to the composition of the feed itself. This temperature value would account for the boiling point elevation produced by the pressure prevailing in the column with the required boil-up rate. Composition Control System IV, described in Chapter IV, was utilized in all cases. Drawing 9 shows the flow diagram and the arrangement of the instrumentation in the rectifying column.

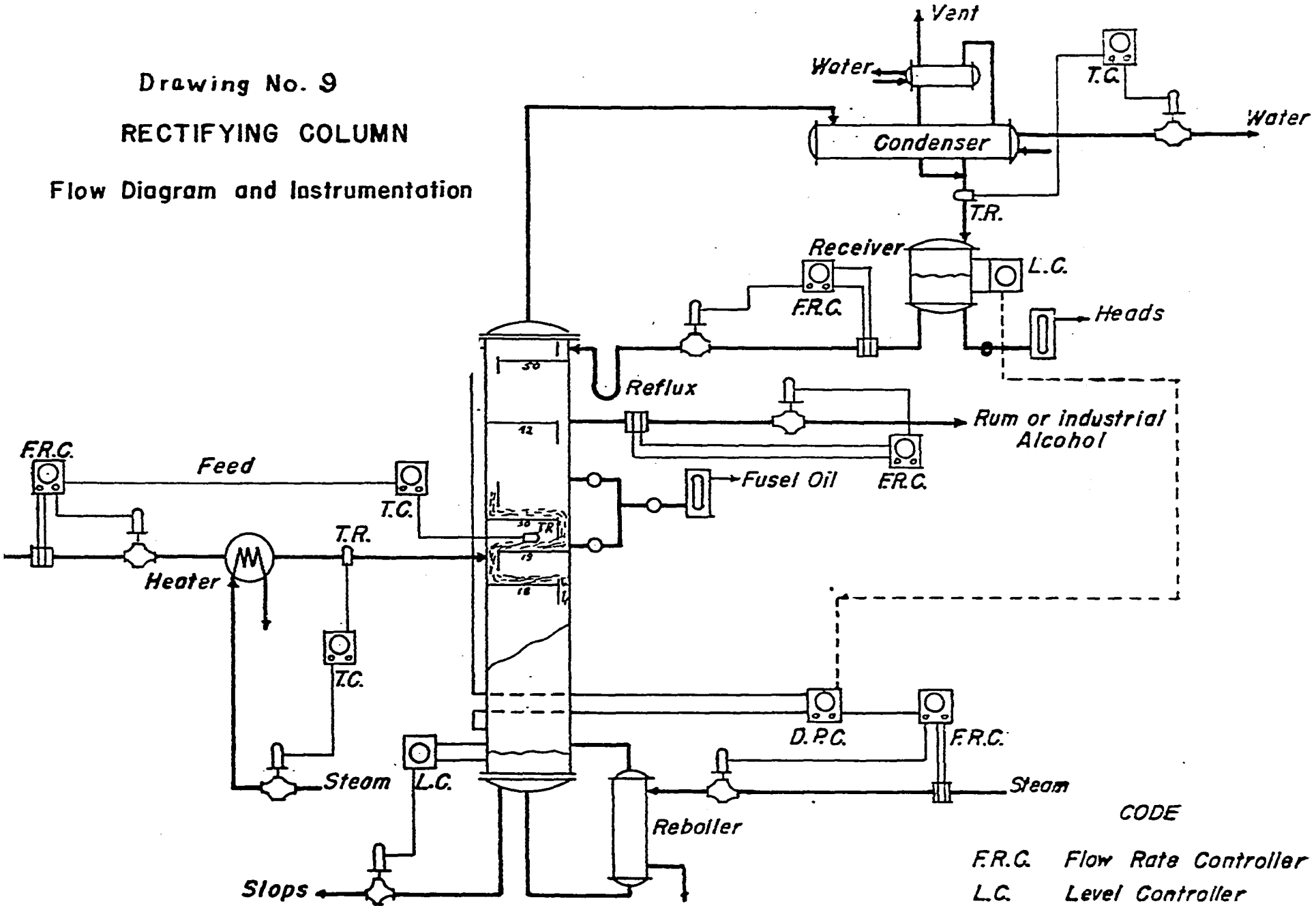
In Table 8 the values of the operating variables for the rectifying column in each experiment are shown. Besides the alcohol content in the feed and the reflux ratio utilized, values are given for the rates of flow of the feed, heads, reflux, main product and fusel oil streams. Control reference temperature, plate of main product take-off, feed plate and the numbers of the tables in the Appendix presenting the data obtained in each experiment are also indicated.

The "heads" stream of the rectifying column contained in all cases about 3% of the alcohol fed to the column. Plate 18 was the feed plate in

Drawing No. 9

RECTIFYING COLUMN

Flow Diagram and Instrumentation



CODE

F.R.C.	Flow Rate Controller
L.C.	Level Controller
T.C.	Temperature Controller
T.R.	Thermometer
D.P.C.	Differential Pressure

TABLE 8

OPERATING CONDITIONS IN THE RECTIFYING COLUMN IN THE VARIOUS EXPERIMENTS CONDUCTED AT DIFFERENT REFLUX RATIOS AND FEED COMPOSITIONS

Feed Composition % Alcohol by Volume	Reflux Ratio	Nominal Feed Rate Gal/Hr..	Reflux Rate Gal/Hr.	Main Product Rate Gal/Hr.	Heads Rate Gal/Hr.	Fusel Oil Side-stream Rate Gal/Hr.	Ref. Temp. °F	Plate of Main Product Take-off	Feed Plate	Tables Showing Experimental Data
20	5:1	70	75	15	0.5	0.5	194.5	42	18	XVI, XVII
20	4:1	75	64	16	0.5	0.5	194.5	42	18	XVIII, XIX
20	3:1	75	48	16	0.5	0.5	193.0	42	18	XX, XXI
20	2:1	85	40	20	0.6	0.5	190.0	46	18	XXII, XXIII
30	15:1	22	90	6	0.2	0.3	191.0	42	18	XXIV, XXV
30	10:1	35	100	10	0.4	0.5	191.0	42	18	XXVI, XXVII
30	5:1	50	75	15	0.5	0.5	192.0	42	18	XXVIII, XXIX
30	4:1	65	80	20	0.6	0.5	191.0	42	18	XXX, XXXI
30	3:1	65	60	20	0.6	0.5	192.0	42	18	XXXII, XXXIII
30	2:1	65	40	20	0.6	0.5	188.0	46	18	XXXIV, XXXV
40	5:1	38	75	15	0.5	0.5	190.0	42	18	XXXVI, XXXVII
40	4:1	50	80	20	0.6	0.5	190.0	42	18	XXXVIII, XXXIX
40	3:1	50	60	20	0.6	0.5	190.0	42	18	XL, XLI
40	3:1	50	60	20	0.6	0.5	190.0	42	18	XLII, XLIII
40	3:1	50	60	20	0.6	0.5	190.0	42	18	XLIV, XLV
40	2:1	50	40	20	0.6	0.5	189.0	46	18	XLVI, XLVII
50	5:1	30	75	15	0.5	0.5	186.0	42	18	XLVIII, XLIX
50	4:1	40	80	20	0.6	0.5	188.0	42	18	L, LI
50	3:1	40	60	20	0.6	0.5	188.0	42	18	LII, LIII
50	2:1	40	40	20	0.6	0.5	189.0	46	18	LIV, LV
60	5:1	30	100	20	0.6	0.5	187.5	42	18	LVI, LVII
60	2:1	30	40	20	0.6	0.5	182.0	46	18	LVIII, LIX, LX

all experiments. The main product was removed from plate 42 in all cases except when reflux ratios of 2:1 were utilized. Under the latter conditions plate 46 was the take-off plate in order to get a product of at least about 180°P. In all experiments the column was run for 24 hours after withdrawal of product commenced. Samples were taken from plates 50, 42, 38, 34, 30, 26, 24, 23, 21, 20, 19, 18, 17, 16, 15, 14, 12, 8 and 4 at 0, 3, 6, 9, 12, 15, 18, 21, and 24 hours after withdrawal of main product commenced. Plates are numbered from bottom up. Numerous consecutive plates around the feed plate were selected since the information available in the literature and the results of our preliminary experiments indicated that the fusel oil band locates itself in this region except for the cases when reflux ratios of 2:1 are utilized. With reflux ratios of 2:1 no apparent sharp accumulation occurs and, accordingly, the sampling plates were chosen evenly along the column. In this case, samples were taken from plates 50, 46, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 22, 18, 16, 14, 10, 6 and 2, at the same time intervals mentioned above.

In the few instances in which mechanical difficulties produced some momentary instabilities shortly before sampling times, the set of samples corresponding to that particular period was discarded. All samples were analyzed for apparent alcohol content utilizing the hydrometer method. Fusel oil was determined by the Rum Pilot Plant modification of Komarowsky's colorimetric method given in Chapter III. Pretreatment of the samples was found not to be necessary for our purposes.

Temperature readings were taken every hour from plates 50, 48, 46, 44, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 23, 22, 21, 20, 19, 16, 14, 12 and 6.

No fusel oil side stream was removed during the first 12 hours of operation in order to allow a continuously increasing accumulation of fusel oil in the column. Hence, sampling at different time intervals during this period gave fusel oil distribution data at different values of maximum concentration in the plate of peak accumulation. After taking the 12th hour samples, withdrawal of fusel oil was commenced from the plate where, according to the analyses of the 9th hour samples, the maximum concentration was found. A fusel oil take-off of 0.5 gallons per hour was used in all cases since, as has been mentioned in preceding sections, there is no method available which would allow an instantaneous determination of fusel oil content in the take-off plate just before beginning the removal of the oil stream with the purpose of establishing the rate of flow of the latter by material balance. The only exception to this was the experiment in which a reflux ratio of 15:1 was used. In this case the rate of feed, and consequently the amount of fusel oil entering the column, was too low. A side-stream of 0.3 gallons per hour was utilized.

The size of the fusel oil side-stream, relative to its fusel oil content and that of the feed, determines if the oil accumulation in the column will either increase or decrease after withdrawal of the side-stream has commenced in order to establish an oil balance. Sudden variations in the concentration of fusel oil in the feed will produce corresponding changes in the accumulation of the oil in the column. In our case, variations in the fusel oil content of the feed from time to time were most likely since very frequently the fermented mash entering the distillation process for a given experiment proveined from a number

of fermenters where, in turn, fermentation experiments were being conducted under different conditions. For our purposes, however, variations in the fusel oil accumulation in the column after withdrawal of the oil stream commenced was rather advantageous since it permitted the gathering of distribution data at a greater variety of peak concentration values for each particular set of operating conditions.

RESULTS

Tables XVI through XXIII, in the Appendix, present the results obtained in the group of experiments conducted with a 20% alcohol feed. For each experiment two tables are given. The first table shows the fusel oil distribution by plates of the column at different time intervals while the second shows the apparent alcohol content in the same samples. The data of alcohol distribution serves to confirm the excellent stability prevailing in the column during the course of the different experiments. These data do not give the true alcohol content for the intermediate plates of the column where considerable concentrations of fusel oil are present, with the consequent introduction of deviations. Toward the ends of the column, where fusel oil concentrations are very low, the error introduced would be negligible. True values can be easily obtained, when required, from the graphs presented in Chapter IV. The tables in the Appendix, however, give the apparent values because it is felt that they will be more useful in the control of actual operations in a distillery. The tables presented include the alcohol and fusel oil content of composite samples of the feed, "heads" and main product.

From the data obtained it can be observed that the plate of maximum concentration of fusel oil corresponds to plates 21, 22 and 24 when utilizing reflux ratios of 5:1, 4:1 and 3:1, respectively. No definite

accumulation of fusel oil occurs when utilizing a reflux ratio of 2:1.

Only one peak of concentration was found to occur and this appears on the rectifying section a few plates over the feed plate, the exact location depending on the reflux ratio utilized. The plate of maximum concentration remains the same throughout the duration of the operation. Plates adjacent to that of peak accumulation have fusel oil concentrations similar to the latter becoming in some instances equal within the limits of accuracy of the analytical method. The width of the fusel oil band as well as the fusel oil content in the upper trays of the column at similar maximum concentrations on the fusel oil take-off plate, depends on the reflux ratio utilized.

The concentration of fusel oil at plates of similar alcohol content is not similar, but depends on the reflux ratio being utilized. This will be discussed in detail in later paragraphs.

Very small concentrations of fusel oil were found in the lower plates of the column in all cases. In one particular experiment no fusel oil at all was found in the lower plate samples, i.e., plate 4 from bottom up, at any period of time.

Much greater accumulations were obtained with a reflux ratio of 5:1 than with 4:1, even though about the same amount of fusel oil was leaving with the main product and the heads in both cases, due to the fact that the feed in the first case contained about 1.5 times as much fusel oil as the second. In the experiment in which a 3:1 reflux ratio was used the feed contained about the same concentration of fusel oil as in the 5:1 case. The main product in the 3:1 case, however, contained much more fusel oil than in the 5:1 experiment and, therefore, smaller

accumulations were produced in the former since greater amounts of the oil were leaving the column with the main product.

The results presented indicate that the withdrawal of a fusel oil side-stream does not cause any displacement in the distribution of fusel oil.

With a reflux ratio of 2:1 very interesting results were obtained. Under these conditions the fusel oil band is very wide and no definite peak occurs. The oil content in the upper trays of the column, and consequently in the main product, is very high. In the lower plates of the column, however, the presence of fusel oil is as low as when higher reflux ratios are used. This suggests that the steam distillation effect is probably the only factor determining the concentration of fusel oil in the alcohol-exhausted plates. It can be observed from the data that, even in the 0 hour samples, there is no evidence of fusel oil accumulation. This indicates that the accumulation that is undoubtedly produced during the total reflux period is promptly destroyed when withdrawal of product and "heads" commences. Actually, there is an inevitable time lag between the moment when removal of product and "heads" commences and the moment when samples are taken. The latter were collected only when the unstabilities produced by the transition from total reflux operation to steady state operation with the removal of products, were overcome. The time lag is usually of the order of 30 minutes.

Tables XXIV through XXXV in the Appendix present the results obtained in the group of experiments conducted with a 30% alcohol feed. Again, the distribution of fusel oil and alcohol by plates of the column

are given for each experiment. With this particular feed composition, reflux ratios of 15:1 and 10:1 were studied in addition to the 5:1, 4:1, 3:1 and 2:1 runs.

The results obtained follow the same lines of those obtained with a 20% alcohol feed. The observations made in the first group of experiments were totally confirmed.

Only one concentration peak was formed. As before, it occurs in the lower plates of the rectifying section above the feed plate and its exact location varies with the reflux ratio utilized. The plate of maximum concentration does not change during the course of the operation. The removal of the fusel oil side-stream does not produce any shift in the fusel oil band. Changes in the width of the fusel oil band with different reflux ratios become evident in this group of experiments in which a rather wide range of reflux ratios was studied. As an example of this, the following list gives approximate values to which the fusel oil concentrations had dropped at plate 30 using different reflux ratios and when the fusel oil concentration in the plate of maximum accumulation was of the order of 11,000 mg. per 100 ml. It should be remembered that plate 18 was the feed plate in all cases.

Reflux Ratio	Approximate Concentration of Fusel Oil at Plate 30, mg. per 100 ml.
15:1	200
10:1	500
5:1	1,200
4:1	2,500
3:1	5,000

Accordingly, the concentration of fusel oil in the upper plates of the column varied markedly with reflux ratios. The following concentrations were obtained in composite samples of the "heads" stream and the main product at different reflux ratios.

Reflux Ratio	Fusel Oil Content, mg. per 100 ml., Heads	Main Product
15:1	5	5
10:1	5	10
5:1	10	20
4:1	20	35
3:1	20	135
2:1	40	370

The results obtained show that, as in the previous group of experiments, the content of fusel oil by plates is not only a function of the alcohol content of the plate, but also greatly dependent on the reflux ratio utilized.

The absence of fusel oil from alcohol-exhausted plates was even more marked in this group of experiments.

Maximum concentrations from about 10,000 to 13,000 mg. per 100 ml. were produced in the plates of peak accumulation. These values varied, again, according to the relative sizes and fusel oil content of the feed, "heads", main product and oil side-stream. The results indicate that with the higher reflux ratios greater differences in fusel oil content are obtained between the plates of peak accumulation and those adjacent to it. With lower reflux ratios the fusel oil band is flatter.

As in the case of the 20% alcohol feed, no definite accumulation

is produced utilizing a reflux ratio of 2:1. The oil distributes more or less evenly along the large central portion in the column and very high contents are produced in the main product. Even with the wide and flat fusel oil band obtained, fusel oil was completely absent from the alcohol-exhausted plates in the bottom of the column.

Tables XXXVI through XLVII present the results of the group of experiments conducted with a 40% alcohol feed. The results confirm the observations of the two previous groups. The plate of maximum accumulation was plate 20, 21 and 22 for reflux ratios of 5:1, 4:1 and 3:1, respectively. No definite accumulation was produced with a reflux ratio of 2:1. In one particular experiment very low concentrations of fusel oil were present in the alcohol-exhausted lower plates of the column. In all other cases fusel oil was absent from the bottom end of the column.

Two special experiments were conducted at reflux ratios of 3:1 and 40% alcohol feed. In one case the fusel oil content was adjusted to about one half the value found in the regular experiment at 3:1 reflux ratio. In the second special experiment, concentrated fusel oil was added to the raw distillate from the beer column to produce a fusel oil concentration approximately twice that naturally obtained in the regular experiment. The purpose of these two special runs was to determine experimentally the effect of differences in the fusel oil content of the feed on the fusel oil band. The results indicate that in the three experiments run at a reflux ratio of 3:1 and a 40% alcohol feed, the plate of maximum fusel oil accumulation was plate 22 in all cases. Maximum accumulations of about 4000 mg. per 100 ml. were produced in the case in which the fusel oil

content of the feed was 30 mg. per 100 ml. When the feed contained 70 mg. of fusel oil per 100 ml., the maximum accumulation produced was of the order of 9,000 mg. per 100 ml. In the case in which the feed was strengthened in its fusel oil content to 140 mg. per 100 ml., maximum concentrations of the order of 15,000 mg. per 100 ml. were produced in the plate of peak accumulation. The concentration of fusel oil in the various plates of the column is definitely affected by that of the plate of peak concentration, but no simple linear relation exists. The effect is largely noticed in the central portion of the column. The lower 16 plates of the column were virtually unaffected. Small variations can be noticed in the top 8 trays of the column.

Tables XLVIII through LV present the results of the group of experiments conducted with a 50% alcohol feed. Although--as is also the case with all previous runs--each experiment provides alcohol and fusel oil distribution data which is characteristic of the particular set of operating conditions used, the general observations pointed out previously regarding the behavior of fusel oil, were totally confirmed. Peak accumulations occurred at plate 20 when utilizing reflux ratios of 5:1 and 4:1, while it was found to occur at plate 21 when operating at a 3:1 reflux ratio. Although peak accumulations occurred at the same plate when 5:1 and 4:1 reflux ratios were utilized, smaller concentrations of fusel oil were produced in the top region of the column when operating with the 5:1 ratio. A somewhat broader band was produced when using a 4:1 ratio. No accumulation was produced when utilizing a 2:1 reflux ratio. Absolute absence of fusel oil in the alcohol-exhausted plates was observed in all cases.

The results obtained in two experiments conducted with 60% alcohol feeds are presented in tables LVI through LX. One experiment was conducted at a reflux ratio of 5:1 with the objective of determining if with the utilization of these operating conditions the peak accumulation of fusel oil would occur below the feed plate. The second experiment was run at a 2:1 reflux ratio with the objective of determining if the greater alcohol content of the feed would produce a significant accumulation of fusel oil in a portion of the column.

The results obtained indicate that at a reflux ratio of 5:1 peak accumulations occur at plate 19, i.e., one plate above the feed plate. Concentrations in the feed plate and below are noticeably lower probably due to the diluting effect of the feed itself. With a reflux of 2:1 definite accumulation of fusel oil was found to occur, which shows once more that the behavior of fusel oil in the column would not be only a function of the reflux ratio used but also of the alcohol content of the feed. The fusel oil band produced is, however, very broad resulting in relatively high fusel oil contents in the upper trays of the column and consequently in the main product and in the "heads". Peak accumulations occur around plates 22 to 24. The relative distribution of compositions obtained is, in general, less defined and steady than when ratios of 3:1 or higher were utilized with any feed composition. In both experiments fusel oil was not found in the alcohol-exhausted plates of the column. Table LX, in the Appendix, presents a tabulation of temperature values prevailing in several plates along the rectifying column during the course of the experiment conducted with a 60% alcohol feed and a reflux ratio of

2:1. It can be observed from the data that temperature values were practically constant at each plate during the course of the run. The excellent stability shown by Table LX is typical of that obtained in all cases.

Tables 9, 10 and 11 summarize some of the results obtained in the course of our experiments. In Table 9, the location of peak accumulations under different operating conditions is given in terms of number of trays above the feed plate. The combined effect of feed composition and reflux ratio can be readily observed. Table 10 gives the concentration of fusel oil in the product under different operating conditions while Table 11 gives corresponding values for the top plate of the column.

TABLE 9

LOCATION OF PLATE OF MAXIMUM FUSEL OIL CONCENTRATION UNDER DIFFERENT OPERATING CONDITIONS, PLATES ABOVE THE FEED PLATE

% Alcohol by Volume in Feed at 60°F	Reflux Ratio					
	2:1	3:1	4:1	5:1	10:1	15:1
20	No acc.	6	4	3	-	-
30	No acc.	5	3	3	2	2
40	No acc.	4	3	2	-	-
50	No acc.	3	2	2	-	-
60	4-6	-	-	1	-	-

TABLE 10

FUSEL OIL CONTENT IN MAIN PRODUCT UNDER DIFFERENT OPERATION CONDITIONS
MG. OF FUSEL OIL PER 100 ML. OF SAMPLE

% Alcohol by: Vol. in Feed: at 60°F	Reflux Ratio					
	2:1	3:1	4:1	5:1	10:1	15:1
20	450	120	45	45	--	--
30	370	135	35	20	10	5
40	350	85	25	15	--	--
50	260	60	25	15	--	--
60	200	--	--	15	--	--

TABLE 11

FUSEL OIL CONTENT IN TOP PLATE OF THE RECTIFYING COLUMN
UNDER DIFFERENT OPERATING CONDITIONS,
MG. OF FUSEL OIL PER 100 ML. OF SAMPLE

% Alcohol by: Vol. in Feed: at 60°F	Reflux Ratio					
	2:1	3:1	4:1	5:1	10:1	15:1
20	150	20	20	20	--	--
30	55	20	20	15	5	5
40	65	10	10	5	--	--
50	55	10	15	10	--	--
60	35	--	--	5	--	--

CONCLUSIONS

From the results of this work the following conclusions may be drawn:

1. The point in the column where maximum accumulations of fusel

oil occur is a function of the reflux ratio utilized and the alcoholic strength of the feed. At any given alcoholic content in the feed, the higher the reflux ratio utilized the lower the location of the plate of maximum fusel oil concentration. The data presented covers the most common range of operating conditions in commercial practice and can be used to determine the plate of fusel oil take-off relative to the feed plate. The 50 plate column utilized in these studies is typical of those utilized in industrial practice.

2. Under the operating conditions studied, a single peak of fusel oil concentration occurred in all cases. The latter was always found to occur above the feed plate. This finding confirms the theoretical considerations presented in Chapter V when discussing the distribution curve given by Robinson and Gilliland and credited to Barbet, which indicates the occurrence of two peaks of maximum concentration, one above and one below the feed plate (314). It was indicated that in the operation represented by Barbet's data, feed containing 40% alcohol by volume was introduced into the column in the plate where the alcohol content of the liquid was 80% by volume. Should the feed have been added at the plate containing 40% alcohol, it seems that the maximum accumulation would have been produced above the feed plate. The region of low fusel oil content between the two peaks may be attributed to the diluting effect of the feed.

3. Peak concentrations of fusel oil occur where the apparent alcoholic content of the liquid phase of the plate is generally from about 130° to 140°P. Table 12 shows typical values of apparent alcohol content in the plate of peak accumulation under various operating conditions when the concentration of fusel oil in the latter is of the order of 10,000 mg. per 100 ml.

TABLE 12

APPARENT ALCOHOL CONTENT IN THE PLATE OF MAXIMUM FUSEL OIL CONCENTRATION

% Alcohol by Vol. in Feed at 60°F	Reflux Ratio				
	3:1	4:1	5:1	10:1	15:1
20	138-145	139-141	135-137	--	--
30	131-132	131-135	133-135	130-131	130-134
40	134-137	132-136	130-132	--	--
50	136-137	135-137	139-142	--	--
60	--	--	135-137	--	--

4. The results presented indicate that the width of the fusel oil band is a function of the operating conditions utilized. At any alcoholic content in the feed, higher reflux ratios produced narrower fusel oil bands. These resulted in greater differences in fusel oil content between the plate of maximum accumulation and those adjacent to it. In addition, lower fusel oil contents were produced in the upper trays of the column and consequently in the product and "heads" streams. It should be pointed out here that the nature of the constituents of the fusel oil present in any particular case, would play an important part in this respect. A raw distillate containing isopropyl alcohol, whose volatility is very close to that of ethanol, as a significant constituent of the fusel oil present, would yield higher concentrations of fusel oil in the top of the column than a raw distillate in which isopropyl alcohol is present in very small amounts, even if in the latter case a somewhat lower reflux ratio is utilized. In our case, we had much greater variations in the composition

and concentration of the fusel oil present in the raw distillates than it would be expected in industrial practice. The reason for this situation is that our fermented mash was the product of fermentation experiments in which a wide variation of fermenting conditions were employed. It was pointed out in Chapter I that the composition and concentration of fusel oil in any particular case would depend on the conditions utilized in the fermentation process. In spite of this fact, the data shown in Tables 10 and 11, as well as that on the individual experiments presented in the Appendix, indicates definite trends regarding the effect of reflux ratios on the content of fusel oil in the upper region of the column. The few deviations found in Tables 10 and 11 are of the order of 5 to 10 milligrams of fusel oil per 100 milliliters of sample. These may be partly attributed to differences in the composition of the oil being handled and to the inherent limitations of the analytical method.

5. A very interesting observation, confirmed throughout the course of all our experimental work, is that the fusel oil content at plates of similar alcohol content is not necessarily similar, even when similar fusel oil concentrations are present in the plate of maximum accumulation and feeds of the same alcohol content are used, but depends largely on the reflux ratio being utilized. This fact is of great importance in the production of alcoholic beverages where, very often, the alcohol content of the liquid is used as criteria for establishing the main product take-off plate. These points can be illustrated by the following data which indicate the fusel oil content in liquids having about 175°P. The data is taken from the group of experiments in which feed containing 40% alcohol by volume was used. The fusel oil content in the plate of peak

concentration was about 10,000 mg. per 100 ml. in all cases.

Reflux Ratio	Fusel Oil Content in Plate Containing Liquid at 175°P	Plate Number
5:1	2,350	26
4:1	1,350	30
3:1	500	34

The explanation for this behavior follows from the figures given in the column showing the plate number where the desired concentration occurred. At lower reflux ratios the desired alcoholic strength is attained at a higher plate in the column where the fusel oil concentration has dropped to a greater extent. This indicates that the separation of fusel oil does not depend solely on the alcohol enrichment of the liquid. The reflux ratio utilized has a definite effect. There are two opposing effects involved which are as follows: By increasing the reflux ratio the fusel oil band is narrowed, should other conditions remain the same. On the other hand, in so doing, any given alcoholic strength would be obtained at a lower plate in the column closer to the greatest accumulations of fusel oil. At the upper section of the column a smaller variation in the alcohol content by plate will be produced with a given change in reflux ratio. Accordingly, in any particular case the selected alcoholic strength value would determine the effect of using different reflux ratios on the fusel oil content of the product. The following data, taken from the group of experiments run with a 30% alcohol feed, illustrates these points. The values given below correspond to fusel oil concentrations found in plates whose liquid contained about 188°P when the fusel oil

content was about 10,000 mg. per 100 ml.

Reflux Ratio	Fusel Oil Content in Plate Containing Liquid at 188°P	Plate Number
15:1	35	34
10:1	60	34
5:1	80	38
5:1	90	42

The tables of data presented in the Appendix under different operating conditions may be used advantageously in the selection of these operating conditions.

6. The resluts of our experiments proved that variations in the concentration of fusel oil in the feed with a definite size of fusel oil stream, would vary the magnitude of fusel oil accumulation in the column, but will not produce a displacement in the location of the plate of maximum concentrations.

7. It may be observed from the data presented in the Appendix, that in many instances a given increase in the concentration of fusel oil in the plate of maximum accumulation does not produce, the reflux ratio and the composition of the feed remaining unchanged, a proportional increase in the fusel oil content of the plates in the top and bottom regions of the column. After certain values are reached at the plate of peak concentration, an increase in the latter usually results in a proportionally smaller increase in the upper and bottom trays. This is explained by the fact that the fusel oil accumulated in the different regions of the column varies in composition. That accumulating in the

upper trays consists mostly of the more volatile higher alcohols, principally isopropanol, if present. During the course of continuous operations without the removal of a fusel oil side-stream, a relatively smaller portion of the most volatile constituents entering with the feed will accumulate in the column since they will account for the greater part of the fusel oil leaving with the main product and with the "heads" stream. Accordingly, the oil continuously accumulating in the column while operating without removing a fusel oil side-stream, or when the size of the latter is too small, consists to a greater extent of the higher boiling constituent alcohols which are forced down by the rectifying action taking place in the column and which tend to accumulate at a lower region of the latter. Greater accumulations in the middle plates of the column certainly affect that of the upper section, but this effect would be greater should all the most volatile constituents of fusel oil remain in the column instead of leaving with the top products in much greater proportions than the less volatile. As should be expected, the effect discussed above is more noticeable with higher reflux ratios since the latter decreases the content of higher boiling constituents in the fusel oil present in the upper trays of the column.

8. Reflux ratios of 2:1 or below do not produce predominant accumulations in any region of the column with feeds of alcoholic strengths up to 50% alcohol by volume. Products very high in fusel oil content are obtained. When feed containing 60% alcohol by volume was processed under a 2:1 reflux ratio, a broad band of fusel oil concentrations was produced which resulted in a product very high in fusel oil content.

9. Fusel oil was not present in any case in the alcohol-exhausted plates in the lower region of the column. When no definite accumulation of fusel oil occurred with the lower reflux ratios studied, the oils distilled over with the "heads" and main product stream giving bottoms free from higher alcohols. In all cases, fusel oil-free samples from the bottom and from few trays above the reboiler, possessed the characteristic "tails" odor frequently attributed to fusel oil and which is evidently due to unidentified impurities.

10. The experimental data obtained in the course of this work can be advantageously utilized in the design of equipment and in the selection of operating conditions for any given product specifications.

CHAPTER VIII

COMPILATION OF EQUILIBRIUM DATA FOR THE SYSTEM ETHANOL-WATER AT ATMOSPHERIC PRESSURE

In the course of experimental investigations on several phases of alcoholic distillation, the need was felt for tables which would present, in a single compilation, liquid-vapor equilibrium data for the system ethanol-water expressed in mole fraction, per cent by weight and per cent by volume, allowing direct conversion between these terms. The term per cent by volume in the vapor phase refers to the condensate obtained after the vapor is totally condensed.

Equilibrium data for the system ethanol-water at atmospheric pressure have been determined by Evans (362), Rayleigh (369), Sorel as given by Elliot (361), Bergstrom as given by Hausbrand (363), Blacher as given by Hausbrand (364), Carey and Lewis (359), and Cornell and Montonna (360).

The data of Cornell and Montonna and that of Carey and Lewis are the most recent and are generally accepted as the most accurate. The agreement between the two sets of data is excellent and both are extensively used in works on the subject (358, 370, 368). Cornell and Montonna utilized in their experimental work the method of Rosanoff, Bacon and White which consists of determining the composition of several fractions of distillate from a liquid of known original composition (371). The percentage compositions for different total weights of distillate are then calculated assuming that the fractions were combined successively. Finally, extrapolating back to zero weight of distillate the composition

of the first infinitesimal fraction of vapor evolved from the liquid, which gives the desired vapor composition, is obtained.

Carey and Lewis utilized the method of Othmer which involves continuous recycling of distillate to the equilibrium still until steady conditions have been established (367). From that moment on the composition of the distillate returning to the still is the same as the composition of the vapors leaving the still. Samples are withdrawn simultaneously from the still and from the condensate chamber and their composition determined, thus yielding the desired liquid-vapor equilibrium compositions.

The fact that such an excellent agreement was obtained between the data of Cornell and that of Carey while utilizing different techniques seems to indicate that these results are highly accurate. The data of Cornell was selected as the basis for the preparation of the tables presented in this work for the reason that it comprises 45 experimental points covering the whole range of compositions while that of Carey comprises only 14, and does not go beyond the azeotropic point.

The compositions of the liquid in terms of per cent by weight were converted into mole fractions by calculation and into compositions by volume at 60°F and 20°C making use of the tables of the U. S. Bureau of Standards (372, 374).

Equilibrium compositions in the vapor, expressed in mole fractions, were obtained from an equilibrium curve plotted using the coordinates given by Cornell and Montonna of a curve drawn by these authors through their own experimental points (360). These compositions in mole fraction were converted into per cent by weight by calculation and were checked

against readings from a second equilibrium curve plotted using coordinates given by the same authors and based on the same experimental points but expressing composition in per cent by weight. Compositions in the vapor in per cent by weight were converted into per cent by volume in the totally condensed vapor at 60°F and 20°C utilizing again the tables of the Bureau of Standards.

The azeotropic composition given is the generally accepted value of 0.8943 mole fraction (359, 370, 365), which is an average of the values found by Young and Fortey (375) and Wade and Merriam (373).

The boiling temperatures of the ethanol-water mixtures were obtained by graphical interpolation from the data of Noyes and Warfel (366). These data, generally accepted as very accurate, are widely used in journals and text books (358, 359, 365, 368, 370). The experimental results, with few exceptions, fall on a very smooth curve from which graphical interpolations can be readily made. The experimental values around the azeotropic point, from 90 to 100 per cent alcohol by weight, were plotted on a scale of 1 mm. equivalent to 0.001°C. The range between 63.0 and 90.0 per cent by weight was plotted on a scale of 1 mm. equivalent to 0.005°C. The range from 0.0 to 63.0 per cent alcohol by weight was plotted on a scale of 1 mm. equivalent to 0.02°C. The interpolated temperatures are reported to the same decimal place as the experimental data.

The tabulation prepared is presented as Table LXI which will be found in the Appendix.

BIBLIOGRAPHY

BIBLIOGRAPHY

Origin and Composition of Fusel Oil

1. Alexandroff, A., and T. Rudakoff, "Composition of Fusel Oil Obtained During the Distillation of Acorns", J. Russ. Phys. Chem. Soc., 36, 207-19 (1904).

2. Arroyo, R., Studies on Rum, Agri. Exp. Station Uni. of Puerto Rico, Res. Bull. No. 5, 1945. Pp. 119-29.

3. Ibid., Pp. 205-19.

4. _____, "The Fusel Oil in Rum", Rev. agr. ind. com. Puerto Rico, 33, 422-4 (1941).

5. Berthelot, M., Chimie Organique Fondee sur la Synthese, II. Paris: 1860. Pp. 631.

6. Bird, M., "Content of Fusel Oil and Ethereal Salts in Demerara Rum", Intern. Sugar J., 29, 84 (1927).

7. Birun, A. M., "Production of Active Amyl Alcohol from Fusel Oil", Khim. Reterat. Zhur., 2, No. 4, 137 (1939).

8. Boswell, M. C., and J. L. Gooderham, "Composition of Fusel Oil from Beet Molasses", Ind. Eng. Chem., 4, 667-70 (1912).

9. Buchner, E., and J. Meisenheimer, "Chemical Reactions Occurring During Alcoholic Fermentation", Ber., 39, 3201-18 (1906).

10. Cahours, A., "Memoires sur l'Huile de Pomme de Terre et ses Combinaisons", Ann. Chim. Phys., 70, 181 (1839).

11. Castor, J. G. B., and J. F. Guymon, "On the Mechanism of Formation of Higher Alcohols During Alcoholic Fermentation", Science, 115, 147-9 (1952).

12. Cattaneo, P., A. Iacobacci, G. Karman de Sutton, and A. R. Lynch, "Chemical Composition in Fatty Acids of a Grape Fusel Oil", Anales Asoc. Quim. Argentina, 40, 150-9 (1952).

13. Cattaneo, P., V. L. Greskbin, and G. Karman de Sutton, "The Fatty Acids of Fusel Oil in Corn and Rye Alcohol", Anales Asoc. Quim. Argentina 41, 105-16 (1953).

14. Chancel, G., "Researches su l'Alcohol Propionique", Compt. rend., 37, 410 (1853).

15. Chapman, E. T., "Note on Some Reactions of Alcohol", J. Chem. Soc., 23, 96-8 (1870).

16. Chapman, A. C., and F. A. Hatch, "The Higher Boiling Constituents of a Yugoslavian Fusel Oil", J. Soc. Chem. Ind., 48, 97T-100T (1929).

17. Cherrington, E. H., Standard Encyclopedia of the Alcohol Problem. Westerville: American Issue Publishing Co., 1926. Vol. III, Pp. 1061-62.

18. Claudon, E., and E. C. Morin, "Higher Alcohols in Brandy and the Products of Fermentation of Sugars by Elliptical Yeast", Compt. rend. Acad. Sciences, 104, 1187-89 (1887).

19. Ibid., Pp. 1109-11.

20. Crampton, C. A., and L. M. Tolman, "A Study of the Changes Taking Place in Whiskey Stored in Wood", J. Am. Chem. Soc., 30, 98 (1908).

21. Darco Sales Corporation, Promoting Fermentation Reactions with Activated Carbon, Br. Patent 336,207 (April 2, 1929).

22. Dietrich, K. R., and O. Klammerth, "The Formation of Fusel Oil in the Course of Alcoholic Fermentation", Z. Spiritusind., 64, 160 (1941).

23. Dorfler, M., "From the Chemistry of Fusel Oil", Chem. Ztg., 35, 281 (1912).

24. Dumas, J. B., "Sur la Composition de l'Huile Extraite de l'eau de Vie de Pommes de Terre", Ann. Chim. Phys., 56, 314 (1834).

25. _____, and J. S. Stas, "Seconde Memoire sur les Types Chimiques", Ann. Chim. Phys., 73, 113 (1840).

26. Dutt, S., "Composition of Patent Still Molasses Fusel Oil of Indian Origin. I", Proc. Natl. Acad. Sci. India, 8, 105-9 (1938).

27. _____, "Composition of Patent Still Molasses Fusel Oil of Indian Origin. II", Proc. Natl. Acad. Sci. India, 9, 69-77 (1939).

28. Eckman, F. L., "The Amount of Estimation of Fusel Oil in Spirits", Chem. Zeit., 12, 564-5 (1889).

29. Ehrlich, F., "New Nitrogenous Constituents of Sugar Residues", Z. Ver. Zuckerind., 53, 804-29 (1903).

30. _____, "A Naturally Occurring Isomeride of Leucine", Ber., 37, 1809 (1904).

31. _____, "About the Origin of Fusel Oil", Z. Ver. Zuckerind., 55, 539 (1905).

32. _____, Process of Obtaining Fusel Oil and Its Constituents, Ger. Patent 177,174 (April 1, 1905).

33. _____, "Behavior of Racemic Amino-Acids Towards Yeast", Z. Ver. Zuckerind., 56, 840-60 (1906).

34. _____, "Die Chemischen Vorange der Hefegärung", Biochem. Z., 2, 52-80 (1906).

35. _____, "Fusel Oil Formation by Yeast", Ber., 39, 4072-75 (1906).

36. _____, Process of Manufacturing Fusel Oil and Components of It, Br. Patent 664,020 (March 20, 1906).

37. _____, "Conditions Governing the Formation of Fusel Oil", Ber., 40, 1027-47 (1907).

38. _____, "Conditions Governing the Formation of Fusel Oil", Z. Ver. Zuckerind., 57, 461-82 (1907).

39. _____, "Natural Isomeride of Leucine", Ber., 40, 2538-62 (1907).

40. _____, Making Fusel Oil, U.S. Patent 885,591 (April 21, 1908).

41. _____, "Synthesis of iso-Leucine", Ber., 41, 1453-58 (1908).

42. _____, "The Production of Succinic Acid During Fermentation", Bied. Zentr., 37 197 (1908).

43. _____, "About the Conversion of Tyrosine into Tyrosol", Ber., 44, 139-47 (1911).

44. _____, "Uber die Bildung des Plasmaeiweisses bei Hefen and Schimmelpilzen", Biochem. Z., 36, 447-97 (1911).

45. _____, "Tryptophol a New Product of Amino Acids", Ber., 45, 883-9 (1912).

46. _____, and P. Pistschimuka, "Conversion of Amines Into Alcohols by Yeasts and Moulds", Ber., 45, 1006-12 (1912).

47. _____, and A. Wendel, "Resolution of Racemic Amino Acids by Yeasts", Z. Ver. Zuckerind., 58, 198-222 (1908).

48. _____, and _____, "Resolution of Racemic Amino Acids by Yeasts", Biochem. Zeitsch., 8, 438-66 (1908).

49. Emmerling, D., "Presence of n-Butyl Alcohol in Fusel Oil From Grain", Ber., 35, 694-5 (1902).

50. _____, "Origin of Fusel Oil", Ber., 37, 3535-8 (1904).

51. _____, "Origin of Fusel Oil", Ber., 38, 953-6 (1905).

52. Enders, C., and K. Karnbach, "Composition of Fusel Oil Obtained by Distilling Fermented Wood-Sugar From the Rhienau Process", Z. Spiritusind., 61, 75-6 (1938).

53. _____, and _____, "Composition of Fusel Oil Obtained by Distilling Fermented Wood-Sugar from the Scholler Process", Holz als Roh und Werkstoff, 2, 135-8 (1939).

54. Farbenind, I. G., Fusel Oils by Fermentation of Sugar Solutions Obtained from Peat, Br. Patent 322,029 (Sept. 19, 1928).

55. Farine, A., "The Origin and Influence of the Products of the Alcoholic Fermentation", Tech. Ind. Schweiz. Chem. Ztg., 1926, 178-82 (1926).

56. Fertman, G. I., and V. E. Semevskaya, "The Evaluation of the Quality of Fusel Oil", Spirtovaya Prom., 21, No. 3, 11-3 (1955).

57. Fernbach, A., and E. H. Strange, Fusel Oils, Br. Patent 15,204 (June 29, 1911).

58. Foth, G., The Praxis de Brennereibetriebes auf Wissenschaftlicher. Berlin: 1935.

59. Fusel Oil, Encyclopaedia Britannica. Chicago: Encyclopaedia Britannica, Inc., C 1956. Vol. 9, Pp. 952-3.

60. Fusel Oil, Encyclopedia Universal Ilustrada Europeo-Americana. Barcelona: Hijos de J. Espasa, 1924. Vol. XXV, Pp. 263-4.

61. Fusel Oil, The New International Encyclopedia, Second Edition, New York: Dodd, Mead and Co., 1930. Vol. 9, Pp. 374.

62. Genevois, L,, "Formation of Higher Alcohols and Their Derivatives During Alcoholic Fermentation", Inds. agr. et aliment (Paris), 69, 27-32 (1952).

63. Glimm, E., and F. Stentzel, "The Production of Fusel Oil During the Fermentation of Beer", Z. ges. Brauwesen, 54, 49-55, 57-62, 65-70 (1931).

64. Guymon, J. F., and J. E. Heitz, "The Fusel Oil Content of California Wines", Food Technol., 6, 359-62 (1952).

65. Harden, A., Alcoholic Fermentation, Fourth Edition. New York: Longmans, Green and Co., 1932. Pp. 167-171.

66. Ibid., Pp 174-177.

67. Haywood, E. W., C. L. Emerson, Jr., and W. M. Davies, "Reconverting Alcohol Production from Wartime Raw Materials", Chem. Met. Eng., 51, 135-9 (1944).

68. Heinzelmann, G., "Amyl Alcohol Content of Raw Fusel Oil", Z. Spiritusind., 36, 14 (1913).

69. Hellström, N., "Impurities in Sulfite Alcohol", Suensk Kem. Tid., 55, 161-8 (1943).

70. Houssiau, A., "Alcoholic Fermentation of Amines in Industrial Sugar Substrates", Congr. Intern. Tech. Chim. Ind. Agr., Compt. rend. V Congr., 1, 864-72 (1937).

71. Jacobs, P. B., and H. P. Newton, "Motor Fuels from Farm Products", U.S.D.A. Misc. Pub., 327, December 1938.

72. Jankovic, S., "The Influence of Various Factors on the Production of Fusel Oil During the Fermentation of Molasses", Z. Spiritusind., 51, 105-6 (1928).

73. Jensen, W., "Investigation of Fusel Oil Obtained in the Production of Alcohol from Sulphite Waste Liquor", Paperi ja Puu (Finland), 32B, 329-32 (1950).

74. _____, and P. Rinne, "Fusel Oil Obtained from Sulphite Waste Liquor", Paperi ja Puu (Finland), 34B, 137-9 (1952).

75. Kailan, A., "Fermentation of Amyl Alcohol", Monatsh, 24, 533-67 (1903).

76. Kervegant, K., Rhums et Eaux-de-Vie de Canne. Vannes: Les Editiones Du Golf, 1946. Pp. 196-205.

77. Ibid., Pp. 267-74.

78. Kilp, W., "Formation of Fusel Oil by Barley Malt and Oat Malt", Z. Spiritusind., 57, 219-21 (1934).

79. _____, and R. Deplanque, "At Which Stage of Fermentation Does Formation of Fusel Oil Begin?", Z. Spiritusind., 57, 306-16 (1934).

80. Kino, K., "Palmitic Acid as a Constituent of Fusel Oil", J. Soc. Chem. Ind. (Japan), 31, 749 (1928).

81. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology. New York: The Interscience Encyclopedia, Inc., 1947. Vol. I, Pp. 262-3.

82. Konovalov, S. A., "Selectivity in Capacity of Yeasts to Utilize Nitrogen from Various Amino Acids", Mikrobiologiya, 18, 351-5 (1949).

83. Kurono, K., "The Formation of Fusel Oil by Sake Yeast", J. Coll. Agr. Tokyo, 1, 283-94 (1912).

84. LeBel, J. A., "Formation of Amyl Alcohol in Alcoholic Fermentation", Compt. rend. Acad. Sciences, 96, 1368-70 (1883).

85. LeCouteur, P., J. Kenyon, and T. A. Rohan, "The Isolation of Optically Pure Negative-sec-Butylcarbinol from Fusel Oil", J. Applied Chem. (London), 1, 341-5 (1951).

86. Lindet, L., "Influence of Temperature on the Production of Higher Alcohols", Compt. rend. Acad. Sciences, 107, 182-3 (1888).

87. Long, J. H., and C. E. Linebarger, "American Fusel Oil", Chem. News, 61, 185-7 (1890).

88. Longinov, U. U., and A. A. Pryanishnikov, "Method of Fractionating Fusel Oil and Composition of the Products", Trans. Inst. Pure Chem. Reagents (Moscow), 12, 18-48 (1931).

89. Luce, E., "Composition of a Fusel Oil and Origin of Acids in Alcoholic Fermentation", J. pharm. chim., 22, 136-8 (1920).

90. Lüder, D. E., "Fusel Oil and Methods of Producing It", Z. Spiritusind., 48, 297 (1925).

91. Markwald, W., "Separation of the Amyl Alcohols Contained in Fusel Oil, I", Ber., 34, 479-84 (1901).

92. _____, and A. McKenzie, "Separation of the Amyl Alcohols Contained in Fusel Oil, II", Ber., 34, 485-91 (1901).

93. _____, "Separation of the Amyl Alcohols from Fusel Oil, III", Ber., 35, 1595-1601 (1902).

94. Martin, G., Industrial and Manufacturing Chemestry, Part I, Seventh Edition, Revised. London: The Technical Press Ltd., 1952. Pp. 314.

95. McDermott, F. A., Fusel Oil by Fermentation, U.S. Patent 1,725,084 (August 20, 1929).

96. McIntosh, J. G., Industrial Alcohol, Second Edition. London: Scott, Greenwood and Son, 1923. Pp. 302-4.

97. Morin, E. C., "Production of Normal Amyl Alcohol by Fermentation of Glycerol by Bacillus Butylicus", Compt. rend. Acad. Sciences, 105, 816-18 (1888).

98. _____, "Brandy from a Wine from Charante Inferieure", Compt. rend. Acad. Sciences, 105, 1019-22 (1888).

99. Mumme, P., "Formation of Fusel Oil and Influence of Higher Alcohols on the Quality of Beer", Wochschr. Brau., 41, 137-8 (1924).

100. Neubauer, O., and K. Fromherz, "Über den Abbau der Aminosäuren bie der Hefegärung", Z. Physiol. Chem., 70, 326 (1911).

101. Neuberg, C., and Hildesheimer, "Ueber Zuckerfreie Hefegärungen, I", Biochem. Z., 31, 170-6 (1911).

102. Ogata, Y., and Y. Matsubara, "Composition of Fusel Oil Obtained by Distillation of Fermented Ipomea Batatas", J. Chem. Soc. Japan, Ind. Chem. Sect., 56, 684-7 (1953).

103. Ordonneau, C., "Composition of Brandy from Wine", Compt. rend. Acad. Sciences, 102, 217-19 (1885).

104. Pasteur, L., "On Amylic Alcohol", Compt. rend. Acad. Sciences, 41, 296 (1855).

105. _____, "On Amylic Alcohol", Ann. Chim., 96, 255 (1855).

106. Perard, J., "Destillery Yields", Congr. intern. tech. chim. ind. agr. Compt. rend. V Congr., 1, 802-32 (1937).

107. Perry, J. H., Chemical Engineers Handbook, Third Edition. New York: McGraw-Hill Book Co., 1950. Pp. 130-45.

108. Pierre, I., and E. Puchot, "Researches on the Fermentation of Alcohols", Ann. Chem. Pharm., XIII, 253-295 (1872).

109. Prescott, S. C., and C. G. Dunn, Industrial Microbiology, Second Edition. New York: McGraw-Hill Book Co., 1949. Pp. 160-1.

110. Pringsheim, H. H., "Origin of Fusel Oil", Ber., 38, 486-7 (1905).

111. _____, "Origin of Fusel Oil", Centr. Bakt. Par., 15, 300-12 (1905).

112. _____, "Formation of Fusel Oil in the Acetone-Daver Yeast Fermentation", Ber., 39, 3713-5 (1906).

113. _____, "Nitrogenous Nutrition of Yeast", Biochem. Z., 3, 121-286 (1907).

114. _____, "Action of Bacteria in Fusel Oil Formation", Biochem. Z., 16, 242-5 (1908).

115. _____, "Formation of Fusel Oil by Certain Fungi", Biochem. Z., 8, 128-31 (1908).

116. _____, "The Repression of Fusel Oil Formation and the Action of Bacteria in the Formation of Higher Alcohols in Fermentation", Biochem. Z., 10, 490-7 (1908).

117. Rabuteau, L., "Alcohols in Potato Fusel Oil", Compt. rend. Acad. Sciences, 87, 501 (1878).

118. _____, "De la Presence des Alcohols Isopropylique, Butylique Normal et Amylique Secondaire dan las Huiles et Alcohols de Pommes de Terre", Bull. soc. chim., 33, 178 (1880).

119. Raghunatha-Rao, Y., "Composition of Fusel Oil, Mandya Distillery", Current. sci., 7, 53-4 (1938).

120. _____, "The Higher Boiling Components of Fusel Oil", J. Sci. and Ind. Res. (India), 1, 196-200(1943).

121. Rogers, W. A. C., and R. C. S. Lond, "The Preparation of Active Amyl Alcohol and Active Valeric Acid from Fusel Oil", Trans. Chem. Soc., 63, 1130-5 (1893).

122. Scheckenbach, J., Making Fusel Oil, U.S. Patent 1,118,238 (Nov. 24, 1915).

123. Schilfarth, H., "The Formation of Fusel Oil in Beer", Brauerei Wissenschaftl. Beil., 5, 47-51 (1952).

124. Schoen, M., "The Problem of the Higher Alcohols", Congr. intern. tech. chim. ind. agr., Compt. rend. V Congr., 1, 833-59 (1937).

125. Schrotter, H., "Bases from Fusel Oil", Ber., 12, 1431-2 (1879).

126. Schuphaus, R. C., "Alcohols in Fusel Oil", J. Amer. Chem. Soc., 14, 45-60 (1892).

127. Segal, R. B., "The Influence of Fusel Oils and Their Components on Yeast", Microbiology (USSR), 7, 93-103 (1938).

128. Shichiji, S., Y. Sonada, and T. Hasegawa, "Alcohol Production From Molasses", Hakko Kyokai Shi, 11, 4-8 (1953).

129. Shoruigin, P. P., V. I. Isagulyantz, V. N. Belov, and S. Alexandra, "Composition of High Boiling Parts of Fusel Oil" Ber., 66B, 1087-93 (1933).

130. _____, _____, _____, and Z. D. Aleksandrova, "Investigation of the Residue of Fusel Oil", J. Gen. Chem. (U.S.S.R.), 4, 372-94 (1934).

131. _____, and S. V. Savenkov, "Hydrocarbon Fraction of the Vat Residue of Fusel Oil", J. Applied. Chem. (U.S.S.R.), 9, 1437-41 (1936).

132. Shukla, J. P., and B. D. Kapoor, "Fusel Oil as by-Product of the Alcohol Industry", J. Sci. Soc., India, 2, 42-8 (1953).

133. Sieber, R., "Fusel Oil in Alcohol from Sulfite Waste Liquor", Wochbl. Papierfabr., 51, 2457 (1920).

134. Sultan, A., and I. Stern, "Process for Producing Fusel Oil and Its Constituents", Bull. assoc. chim. sucr. dist., 24, 764-7 (1907).

135. _____, and _____, Process for Producing Fusel Oil and Its Constituents, French Patent 365,619 (Mar. 23, 1906).

136. Swenarton, J., "Higher Alcohols of Fermentation", Science, 70, 554-5 (1929).

137. Taira, T., and T. Masujima, "Unsaponifiable Matter with Higher Boiling Point in Fusel Oil", J. Agr. Chem. Soc. Japan, 10, 232-47 (1934).

138. Thorne, R. S. W., "Nitrogen Metabolism of Yeast. A Consideration of the Mode of Assimilation of Amino Acids", J. Inst. Brewing, 55, (N.S. 46), 201 (1949).

139. Tomada, Y., "Increased Production of Fusel Oil in Alcoholic Fermentation", J. Soc. Chem. Ind. Japan, 42, Suppl. binding, 379-80 (1939).

140. Tomecek, D., "Formation of Fusel Oil During the Production of Alcohol from Molasses", Chem. Zvesti, 5, 231-42 (1951).

141. _____, "Formation of Fusel Oil Manufacturing of Industrial Alcohol from Molasses", Chem. Zvesti, 7, 249-56 (1953).

142. Ubeda, F. B., "High Boiling Components of the Fusel Oil Distillation Residue of Grape Bagasse and Their Commercial Utilization", Anales fis. quim., 37, 356-69, 371-83 (1941).

143. Ullmann, F., Encyclopedia de Quimica Industrial, Segunda Edicion. Barcelona: Editorial Gustavo Gili, S.A., 1931. Vol. IV, Pp. 317-323.

144. Ibid., Pp. 445.

145. Underkofler, L. A., and R. J. Hickey, Industrial Fermentations. New York: Chemical Publishing Co., Inc., 1954. Vol. 1, Pp. 84.

146. Valaer, P., "Foreign and Domestic Rum", Ind. Eng. Chem., 29, 988-1001 (1937).

147. _____, and W. H. Frazier, "Changes in Whisky Stored for Four Years", Ind. Eng. Chem., 28, 92 (1936).

148. Vegezzi, G., and P. Haller, "Constitution of Fusel Oil From Fruits", Mitt. Lebensm. Hyg., 21, 321-5 (1930).

149. Von Einhorn, A., and F. Hollandt, "Ueber die Acylirung der Alkohole und Phenole in Pyridinlosung", Liebig's Annalen, 301, 95 (1898).

150. Webb, A. D., R. E. Kepner, and R. M. Ikeda, "The Composition of a Typical Grape Brandy Fusel Oil", Anal. Chem., 24, 1944-9 (1952).

151. Whitmore, F. C., and J. H. Olewine, "Separation of Primary Active Amyl Alcohol from Fusel Oil by Distillation", J. Am. Chem. Soc., 60, 2569-70 (1938).

152. Windish, K., "On the Composition of Fusel Oil", Arbb. Gesundheitsamt (Berlin), VIII, 1892.

153. Woodman, A. G., Food Analysis, Fourth Edition. New York: McGraw-Hill Book Co., 1941. Pp. 558-60.

154. Ibid., Pp. 580-5.

155. Wurtz, A., "Sur l'Alcohol Butylique", Compt. rend., 35, 310 (1850).

156. Yamada, M., "Furfurole in Fermentation Products", Bull. Chem. Soc. Japan, 4, 31-5 (1929).

157. _____, "Decomposition of Amino Acids by Yeast", J. Agr. Chem. Soc. Japan, 8, 428-32 (1932).

158. Yoshitomi, E., R. Soejima, and M. Imoto, "Fusel Oil from Sweet Potato Brandy", J. Pharm. Soc. Japan, 486, 661-6 (1922).

159. Zakharov, I. P., and P. I. Leshchinskaya, "Formation of Fusel Oil from Technical Leucine", Biokhimiya, 3, 684-93 (1938).

160. Zakharov, I. P., and G. F. Nazarenko, "Using Autoclaved Protein as Nitrogenous Yeast Nutrient and Producing Fusel Oil", Mikrobiologiya, 14, 113-8 (1945).

161. Zalesskaya, M. I., "Obtaining Higher Fusel Oil Yields in Alcoholic Fermentation", Microbiology (U.S.S.R.), 6, 598-615 (1937).

162. _____, "Formation of Fusel Oil During Alcoholic Fermentation", Microbiology (U.S.S.R.), 7, No. 5, 546-64 (1938).

163. _____, "Formation of Fusel Oil During Alcoholic Fermentation", Microbiology (U.S.S.R.), 10, 97-116 (1941).

164. _____, and S. A. Konovalov, "Fusel Oils in the Fermentation of Molasses", Microbiology (U.S.S.R.), 10, 535-8 (1941).

Commercial Uses of Fusel Oil

165. Aleinikov, N. A., "Residual Oil from Rectification of Fusel Oil as a Flotation Reagent", Mineralnoe Suir'e, 5, 1287-9 (1930).

166. A.S.T.M., Standards, Part II, 1946. Pp. 1067.

167. Ayres, E. E., "Amyl Alcohols from Pentanes", Ind. Eng. Chem., 21, 889-904 (1929).

168. Carduck, W., and M. Prager, Wiener Tapetenfabrick Akt.-Ges., Austrian Patent 167,618 (Feb. 10, 1951).

169. Clark, L. H., "High Boiling Solvents from Natural Gas Pentanes", Ind. Eng. Chem., 22, 439-43 (1930).

170. Clark, L. H., "Evolution of a New Chemical Industry", Chem. Met. Eng., 38, 206-10 (1931).

171. Folsch, M., "Fusel Oil and Its Derivatives in the Perfume Industry", Riechstoffind., 4, 51-2, 76-8 (1929).

172. Gregory, T. C., Uses and Application of Chemicals and Other Related Materials. New York: Reinhold Publishing Corporation, 1939. Pp. 296.

173. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology. New York: The Interscience Encyclopedia, Inc., 1947. Vol. I, Pp. 847-9.

174. Kirkpatrick, S. D., "Production of Pure Amyl Alcohols from Gasoline", Chem. Met. Eng., 34, 276-9 (1927).

175. Kozlov, V. N., and V. M. Arashkevich, "Fusel Oil and the Products of Its Reprocessing", Zhur. Pricklad. Khim., 27, 223-5 (1954).

176. Martin, G., Industrial and Manufacturing Chemestry, Seventh Edition, Revised. London: The Technical Press, Ltd., 1952. Part I, Pp. 314.

177. Mellan, I., Industrial Solvents, Second Edition. New York: Reinhold Publishing Corporation, 1950. Pp. 495.

178. Noll, A., "The Behavior of Hydrotropic Mixtures", Chem. Tech. Fabr., 26, 43-6, 47-50 (1929).

179. Perkins, W. H., "The Production and Polymerisation of Butadiene Isoprene, and Their Homologues", J. Soc. Chem. Ind., 31, 622 (1912).

180. Pietrowski, A., "Obtaining of Isovalerianic Acid from Fusel Oils", Przemysl Chem., 13, 413-8 (1929).

181. Rowley, D., H. Steiner, and E. Zimkin, "Use of Amyl Acetate in the Extraction of Penicillin", J. Soc. Chem. Ind., 65, 237 (1946).

182. Snell, F. D., and C. T. Snell, Chemicals of Commerce, Second Edition. New York: Van Nostrand and Co., Inc., 1952. Pp. 226-7.

183. Shukla, J. P., and B. D. Kapoor, "Fusel Oil as by-Product of the Alcohol", J. Sci. Soc., Kanpur (India), 2, 45-6 (1953).

184. Ting, H. W., "Lacker Solvents from Fusel Oil", Chiao-Tung Univ. Res. Inst. Rept. Bur. Chem., 3, 75 (1936).

185. U. S. Tariff Commission, Summaries of Tariff Information, Washington, D.C.: U.S. Government Printing Office, 1948. Vol. I, Part I, Pp. 62-3.

186. Ullmann, F., Encyclopedia de Quimica Industrial, Segunda Edicion. Barcelona: Editorial Gustavo Gili, S.A., 1931. Vol. IV, Pp. 325.

Analytical Methods for the Determination of Fusel Oil

187. Alex, G. L., "Estimation of Alcohols in Fusel Oil", Arch. Pharm., 3, II, 289-300 (1873).

188. Allen, A. H., Commercial Organic Analysis, Fourth Edition. Philadelphia: P. Blakiston's Son and Co., 1912. Vol. I, Pp. 187-203.

189. _____, and W. Chattaway, "Examination of Spirits for Secondary Constituents", Analyst, 102-115 (1891).

190. A.O.A.C., Methods of Analysis, Sixth Edition. Washington: Assoc. of Official Agri. Chemists, 1945. Pp. 196.

191. Bakowski, S., and E. Treszczanowitz, "New Azeotropic Method of Determining the Water Content of Liquids", Przemysl. Chem., 21, 204-8 (1937).

192. Basset, H. P., "To Determine Fusel Oil in Distilled Liquors", Ind. Eng. Chem., 2, 389 (1910).

193. Beckmann, E., "Estimation of Higher Alcohols in Spirits", Zeit. Nahr. Genussm., 10, 143-152 (1905).

194. Bedford, C. H., and R. L. Jenks, "The Determination of Higher Alcohols in Spirits", J. Soc. Chem. Ind., 26, 123 (1907).

195. Beyer, G. F., "Report on the Determination of Fusel Oil in Distilled Spirits", J. Assoc. Offic. Agr. Chemists, 31, 184 (1948).

196. _____, "Report on Aldehydes, Esters and Fusel Oil in Distilled Spirits", J. Assoc. Offic. Agr. Chemists, 33, 314-8 (1950).

197. Bigelow, W. D., "Index to the Literature on the Detection and Estimation of Fusel Oil in Spirits", J. Am. Chem. Soc., 18, 397-402 (1896).

198. Bleyer, B., W. Diemair and E. Frank, "Determination of Higher Alcohols", Z. Untersuch. Lebensm., 66, 389-95 (1933).

199. Bonaterra, R., "Study of the Method of Evaluation of Higher Alcohols by Colorimetric Determination Based on the Furfurol-Sulfuric Acid Reaction", Rev. Fac. Cienc. Univ. Nacl. La Plata, 24, 125-33 (1949).

200. Bouvier, _., "A New Method for Testing Alcohol for Fusel Oil", Zeit. anal. chem., 11, 343 (1873).

201. Budagyon, F., and N. Ivanova, "Determination of Fusel Oil in Spirits", Z. Untersuch. Lebensm., 63, 200-11 (1932).

202. Coles, H. W., and W. E. Tournay, "The Komarowsky Color Reaction for Aliphatic Alcohols. Limitations and Sensitivity", Ind. Eng. Chem., Anal. Ed., 14, 20-2 (1942).

203. _____, and _____, "Removal of Higher Alcohols from Ethanol", Anal. Chem., 19, 936-7 (1947).

204. "Detection of Fusel Oil in Spirits of Wine", N. Repert. Pharm., 22, 118 (1873).

205. Dudley, W. L., "Notes on the Rose Method for the Determination of Fusel Oil and a Comparison of Results by the Allen-Marguardt Method", J. Am. Chem. Soc., 30, 1271-6 (1908).

206. Duke, F. R., "The Komarowsky Reaction", Anal. Chem., 19, 661-2 (1947).

207. Duntze, E., "Quantitative Determination of Fusel Oils in Spirits Containing Oils", Z. Spiritusind., 33, 150 (1910).

208. Dupre, A., "Note on the Examination of Whiskey and Other Spirits for Methylated Spirit and Fusel Oil", Pharm. J. Trans., 3, 867 (1876).

209. Faustein, and Bengs, "The Valuation of Fusel Oil", Chem. Ztg., 33 1057 (1910).

210. Fellenberg, Th. von, "Color Reactions of Aromatic Aldehydes and Their Application in the Analysis of Spirits", Mitt. Lebensm. Hyg., 1, 311 (1910).

211. _____, "Komarowsky Color Reaction", Chem. Ztg., 34, 791 (1910).

212. Foerster, K., "Cause of Jorissen's Reaction for Fusel Oil", Ber., 15, 230-2 (1882).

213. Gierer, S., and O. Hoffman-Oestenhof, "Colorimetric Microtechnique for the Determination of Fusel Alcohols in Fermentation Experiments", Mikrochemie ver. Mikrochim. Acta, 38, 232-6 (1951).

214. Glassenapp, M., "Estimation of Fusel Oil in Rectified Spirits by Rose's Method", Zeit. angw. Chem., 657-63 (1895).

215. Glimm, E., H. Schroder, and F. Stentzel, "Determination of Small Quantities of Fusel Oil", Z. Untersuch. Lebensm., 55, 173-5 (1928).

216. Guymon, J. F., and J. Nakagiri, "Methods for the Determination of Fusel Oil", Proc. Amer. Soc. Enolog., 3, 117-34 (1952).

217. Hager, H., "Qualitative and Quantitative Determination of Fusel Oil", Chem. Centr., 712-714 (1881).

218. Heinzelman, G., "Valuation of Fusel Oil", Z. Spiritusind., 35, 612-3 (1913).

219. Jorissen, A., "Detection of Fusel Oil", Bull. acad. Belg., 50, 108-10 (1880).

220. _____, "Detection of Fusel Oil in Spirit", Bied. Centr., 791 (1881).

221. Katz, L., "Fusel Oil and Esters in Distilled Liquors", J. Assoc. Offic. Agr. Chemists, 2, Part II, 188-96 (1917).

222. Kervegant, K., Rhums et Eaux-de-Vie de Canne. Vannes: Les Editiones Du Golf, 1946. Pp. 396-402.

223. Kilp, W., and B. Lange, "The Determination of the Fusel Oil Content of Alcoholic Solutions Containing a Large Amount of Fusel Oil", Z. angew. Chem., 41, 1163-4 (1928).

224. _____, and R. Buse, "Additional Studies on the Valuation of Fusel Oil", Z. Spiritusind., 60, 305, 310, 312-3 (1937).

225. Komarowsky, A., "Furfuraldehyde and Some Aromatic Aldehydes as a Test for Fusel Oil or Isoamyl Alcohol in Spirits of Wine", Chem. Zeit., 27, 807-8 (1903).

226. Korenmann, J., "About a Color Reaction", Z. anal. chem., 88, 249 (1932).

227. Krauch, C., "Otto's Method for the Estimation of Fusel Oil in Brandy", Bied. centr., 718 (1882).

228. Kreis, H., "Direction for Testing Salicylic Aldehyde Used in the Komarowsky Reaction", Chem. Ztg., 32, 149 (1908).

229. Lampe, B., "Comparing the Values of Raw Fusel Oil by Various Methods", Z. Spiritusind., 51, 30 (1928).

230. _____, and W. Kilp, "Determination of the Fusel Oil Content of Brandy by Rose's Method", Z. Spiritusind., 51, 199-200 (1928).

231. Leithe, W., "Refractometric Fusel Oil Determinations in Potable Spirits", Z. Untersuch. Lebensm., 72, 351-4 (1936).

232. Lemos de Andrade Peres, M. R., "Study of the Official U.S. Method for the Determination of Higher Alcohols in Wines", Anais. inst. vinho Porto, 13, 43 (1952).

233. Lunge, G., V. Meyer, and E. Schulze, "Fusel Oil in Spirit", Chem. Centr., 854-858 (1884).

234. Macoun, J. M,, "Determination of Ethyl Alcohol in Fusel Oil", Analyst, 58, 664-6 (1933).

235. Mann, E.A., and C.E. Tracy, "The Allen-Marguardt Process for the Estimation of Higher Alcohols", J. Chem. Ind., 25, 23 (1907).

236. Marguardt, L., "Estimation of Fusel Oil in Brandy", Ber., 15, 1370-3 (1882).

237. McIntosh, J. G., Industrial Alcohol, Second Edition. London: Scott, Greenwood and Son, 1923. Pp. 12.

238. Mitchell, A. S., and C. R. Smith, "Determination of Fusel Oil by Alkaline Permanganate", U.S.D.A. Bur. Chem. Bull., 122, 199 (1909).

239. Moirano, C., "Los Alcoholes Superiores en las Bebidas Alcoholicas Destiladas", Rev. Fac. Quim. Farm. La Plata, 15, 289-96 (1940).

240. Penniman, W. B. D., D. C. Smith, and E. I. Lawshe, "Determination of Higher Alcohols in Distilled Liquors", Ind. Eng. Chem., Anal. Ed., 9, 91-5 (1937).

241. Peters, R., "Estimation of Alcohol in Fusel Oil", Pharm. Centr., 46, 563-8 (1905).

242. Politzer, A., "Quantitative Determination of Fusel Oil", Chem. Ztg., 36, 1438 (1913).

243. Rocques, X., "Detection of Impurities in Alcohol", Ann. chim. anal., 2, 141 (1897).

244. _____, "Colorimetric Estimation of Higher Alcohols in Brandies", Ann. chim. anal., 10, 103-8 (1910).

245. Rose, B., "Detection of Fusel Oil in Spiritous Liquors", Pharm. Centralb., 27, 5-9 (1885).

246. Ruppin, E., "Determination of Fusel Oil and Aldehydes in Alcoholic Liquors", Z. Untersuch. Lebensm., 62, 215-7 (1931).

247. _____, "Determination of Fusel Oil in Alcoholic Liquors", Z. Untersuch. Lebensm., 66, 389 (1933).

248. Schicktanz, S. T., "Report on Detection of Adulteration of Distilled Spirits", J. Assoc. Offic. Agr. Chemists, 22, 225-6 (1939).

249. _____, and A. D. Etienne, "Determination of Amyl Alcohol Content of Distilled Spirits", Ind. Eng. Chem., Anal. Ed., 11, 390-3 (1939).

250. _____, _____, and W. I. Steele, "Analysis of Fusel Oil by Azeotropic Distillation", Ind. Eng. Chem., Anal. Ed., 11, 420-2 (1939).

251. _____, _____, and J. L. Young, "Correlation of Fusel Oil Values by the Allen-Marguardt and Acetyl Chloride Methods", J. Assoc. Offic. Agr. Chemists, 23, 368-73 (1940).

252. Seelenfried, J., "Determination of the Purity of Spirits", Österreich. Spirituosen-Ztg., 29, 2 (1930).

253. Stutzer, A., and R. Maul, "Estimation of Fusel Oil in Refined Alcohol", Zeit. anal. chem., 35, 159-62 (1896).

254. _____, and O. Reitmair, "Estimation of Fusel Oil in Spirits", Rep. Anal. Chem., 6, 335 (1886).

255. _____, and _____, "Estimation of Fusel Oil in Spirits", Zeit. ang. chem., 522-31 (1890).

256. Takahashi, T., "Detection and Estimation of Fusel Oil", Bull. Coll. Agr. Tokyo, 6, 436-8 (1905).

257. Traube, J., "Estimation of Fusel Oil", Ber., 19, 892-5 (1886).

258. _____, "The Staglagnometer: A New Method for the Determination of Fusel Oil in Spirituous Liquors", Ber., 20, 2644-55 (1887).

259. Uffelman, J., "Estimation of Fusel Oil in Spirits", Dingl. polyt. J., 261, 439-43 (1886).

260. Valaer, P., "Report on Fusel Oil", J. Assoc. Offic. Agr. Chemists, 19, 187-90 (1936).

261. Villforth, F., and W. Schmidt, "Higher Alcohols in Wine", Deut. Weinbau. Wiss. Beihefte, 7, 161-70 (1953).

262. West, D. B., R. F. Evans, and K. Becker, "Studies of the Ester and Higher Alcohol Contents of Beer", Am. Soc. Brewing Chemists, Proc. Ann. Meeting, 51-9 (1951).

263. Woodman, A. G., Food Analysis, Fourth Edition. New York: McGraw-Hill Book Co., 1941. Pp. 569-74.

264. Yamada, M., and K. Takakisi, "Determination of Fusel Oil in Beverages with Vanillin-Sulfuric Acid Reagent", Bull. Agr. Chem. Soc. Japan, 14, 55 (1938).

Separation and Purification of Fusel Oil During Distillation

265. "A Chemical and Metallurgical Flow Sheet--Molasses Distillation", Chem. Met. Eng., 52, 142-5 (1945).

266. "A Modern Destillery", Chem. Met. Eng., 49, 126-9 (1942).

267. Aburai, S., Apparatus for Obtaining Pure Alcohol and Fusel Oil, Japan Patent 174,127 (Nov. 26, 1946).

268. Adams, A. B., "The Distillation of Whiskey", Ind. Eng. Chem., 2, 34 (1910).

269. Arroyo, R., Studies on Rum, Agri. Exp. Station Uni. of Puerto Rico, Res. Bulletin, No. 5, 1945. Pp. 119-22.

270. Ibid., Pp. 129.

271. Barbet, E. A., Fusel Oil From Alcohol Distillation, U.S. Patent 1,389,852 (Sept. 6, 1922).

272. Bohm, O., Means for Recovering Fusel Oil from Continuous Alcohol Stills, Ger. Patent 565,306 (July 21, 1926).

273. Boswell, M. C., and J. L. Gooderham, "Composition of Fusel Oil from Beet Molasses", Ind. Eng. Chem., 4, 667-70 (1912).

274. Brauns, O., "Technical Developments", Svensk Papperstidn., 47, 305-11 (1944).

275. Brelaez, N. J. M., "Distillation of Alcohol", Chem. Eng. Mining Rev., 24, 400 (1932).

276. Bushuen, S. U., and Z. M. Zuanareva, "Washing the Fusel Oil Which Is Withdrawn from Batch Rectification Apparatus", Spirtovaya Prom., 20, No. 1, 28-9 (1954).

277. Carlson, C. S., P. U. Smith, Jr., and C. E. Morrell, "Separation of Oxygenated Organic Compounds by Water Extractive Distillation", Ind. Eng. Chem., 46, 350-6 (1954).

278. Cherrington, E. H., Standard Encyclopedia of the Alcohol Problem. Westerville: American Issue Publishing Co., 1926. Vol. III, Pp. 1060-61.

279. Deutsche Gold-und Silber-Scheideanstalt vorm. Roessler, Recovering Ethyl Alcohol and Fusel Oil from Mixtures, Ger. Patent 625,186 (Feb. 5, 1936).

280. Fertman, G., A. Pokrovskii, and T. Vishnevskaya, "The Effect of Quality of the Raw Spirit on the Products of the Rectification", Spirtovodochnaya Prom., 14, No. 3, 5-12 (1937).

281. Foote, H. E., "The Recovery of Fusel Oil in Philippines", Philippine J. Sci., 25, 405-12 (1924).

282. Fusel Oil, The New International Encyclopedia, Second Edition. New York: Dodd, Mead and Co., 1930. Vol. I, Pp. 353.

283. Ibid., Vol. IX, Pp. 374.

284. Garbarini, G., "Separation of the Fusel Oils", Bull. assoc. chim. sucr. dist., 26, 1078-83 (1909).

285. Glasenapp, M., "Action of Charcoal in the Purification of Spirit", Zeit. angw. chem., Pp. 617-21, 665-72 (1898).

286. Gregor, E., Separation and Purification of Fusel Oil, Ger. Patent 737,534 (June 10, 1943).

287. Grolla, K., "Progress in Practical Rectification Through Modern Research Methods", Branntweinwirt., 73, 386-9 (1951).

288. Hellstrom, N., "Impurities in Sulfite Alcohol", Svensk Kem. Tid., 55, 161-8 (1943).

289. Kawamura, S., S. Tateno, S. Suzuki, and E. Matsui, "A Reconstructed Still Improve Alcohol Quality", Hakko Kyokai-Shi, 9, 38-9 (1951).

290. Kervegant, D., Rhums et Eaux-de-Vie de Canne. Vannes: Les Editions Du Golf, 1946. Pp. 197.

291. Ibid., Pp. 204.

292. Khshanouskii, F. A., "The Rectification of Crude Fusel Oil", Spirtovaya Prom., 20, No. 3, 36-7 (1954).

293. Kiefer, C. J., and E. S. Manohan, Distillation Apparatus for Converting Low Proof Wash Containing Fusel Oil Into High Proof Ethyl Alcohol, U.S. Patent 2,359,860 (Oct. 10, 1944).

294. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology. New York: The Interscience Encyclopedia, Inc., 1947. Vol. I, Pp. 264-7.

295. Krasnitskii, L. D., Separation of Fusel Oil from the Mash Distilling Apparatus, Russ. Patent 52,579 (Jan. 31, 1938).

296. Lampe, B., "Composition of Fusel Oils Which Have Been Separated as Vapor", Z. Spiritusind., 52, 190 (1929).

297. _____, "Further Experimental Results on Fusel Oil Obtained in the Form of Vapor", Z. Spiritusind., 53, 62 (1930).

298. _____, "Separation of Fusel Oil During Rectification", Z. Spiritusind., 52, 389 (1929).

299. _____, and W. Kilp, "Separation of Fusel Oil from First Distillate", Z. Spiritusind., 51, 351-2 (1928).

300. _____, and _____, "Separation of Fusel Oil by the Low Wine Tester", Brennerei-Ztg., 46, 101 (1929).

301. Leonov, P. P., Separation of Furfuraldehyde from Fusel Oil and Amyl Alcohol, Russ. Patent 23,316 (Oct. 31, 1931).

302. Longinov, U. U., and A. A. Pryanishnikov, "Method of Fractionating Fusel Oil and Composition of the Products", Trans. Inst. Pure Chem. Reagents (Moscow), 12, 18-48 (1931).

303. Luhder, E., "Fusel Oil and the Methods of Fusel Oil Recovery", Apparatebau, 38, 163-5, 177-9 (1926).

304. _____, and W. Kilp, "Operating Method of Distilling Apparatus Designed to Produce a High-Proof Alcohol", Z. Spiritusind., 50, 144, 150-2 (1927).

305. Malchenko, A. L., Arrangement for the Separation of Fusel Oils in the Rectification of Alcohol, Russ. Patent 57,866 (Sept. 30, 1940).

306. "Methods of Treating or Processing Heads and Principles of Fusel Oil Separation During Distillation", Amer. Soc. Enol. Proc., 1, 86-100 (1950).

307. McIntosh, J. G., Industrial Alcohol, Second Edition. London: Scott, Greenwood and Son, 1923. Pp. 198-205.

308. Perard, L., "Advisability of Extracting Fusel Oil from Distilling Columns", Chimie and Industrie, Special No., 767 (March, 1932).

309. Pluentsch, F. W., Apparatus for Separating Fusel Oil, Ger. Patent 554,072 (July 6, 1928).

310. Prescott, S. C., and C. G. Dunn, Industrial Microbiology, Second Edition. New York: McGraw-Hill Book Co., 1949. Pp. 225.

311. Rabubeau, L., "Alcohols in Potato Fusel Oil", Compt. rend. Acad. Sciences, 87, 501 (1878).

312. Raghunatha-Rao, Y. N., "Composition of Fusel Oil at Mandya Distillery", Current Sci., 7, 53-4 (1938).

313. Riegel, E. R., Industrial Chemistry, Fifth Edition. New York: Reinhold Publishing Co., 1949. Pp. 399.

314. Robinson, C. S., and E. R. Gilliland, The Elements of Fractional Distillation, Third Edition. New York: McGraw-Hill Book Co., 1939. Pp. 71-80.

315. Sagara, N., and K. Ono, "The Improvement of the Quality of Alcohol", Hakko Kyokai-Shi, 9, 127-32, 165-7 (1951).

316. Shukla, J. P., and B. D. Kapoor, "Fusel Oil as by-Product of the Alcohol", J. Sci. Soc., Kanpur (India), 2, 42-8 (1953).

317. Strauch and Schmidt, Distilling Apparatus, Ger. Patent 648,632 (Aug. 5, 1937).

318. Swallen, L. C., and J. B. Tindall, Purification of Fusel Oil and Amyl Alcohol, U.S. Patent 2,294,346 (Aug. 25, 1943).

319. Thormann, K., "Mode of Action of Distilling Apparatus for High Percentage Spirits", Chem. App., 14, 261-2 (1927).

320. Ullmann, F., Enciclopedia de Quimica Industrial, Segunda Edicion. Barcelona: Editorial Gustavo Gili, S.A., 1931. Vol. IV, Pp. 318.

321. Ibid., Pp. 428.

322. Ibid., Pp. 442-447.

323. Ibid., Pp. 456.

324. Unger, E. D., "Recent Advances in Alcohol Distillation Methods", Chem. Inds., 58, 778-80 (1946).

325. Williams, A. E., "Fusel Oil Elimination in Alcohol as Motor Fuel", Chem. Trade J., 95, 111-12 (1934).

Automatic Controls in the Alcoholic Distillation

326. Bauer, R. L., and C. P. Orr, "Distillation Control Problem; Applications of the McCabe-Thiele Diagram", Chem. Eng. Progress, 50, 312-8 (1954).

327. Boyd, D. M., "Fractionation Instrumentation and Control", Pet. Refiner, 25, 187-91 (1946).

328. _____, "Fractionation Instrumentation and Control", Pet. Refiner, 27, 594-7 (1948).

329. Brown, G. G., and Assoc., Unit Operations. New York: John Wiley and Sons, Inc., 1951. Pp. 262-5.

330. Ibid., Pp. 337.

331. Cahill, J. T., and G. W. Janducck, Device for Controlling Liquid Level and Heating Within a Fractionator, U.S. Patent 2,598,036.(May 27, 1952).

332. Compagnie Francoise de Rattinage, Controlling Distillation, Br. Patent 496,168 (Nov. 25, 1938).

333. Gerhold, C. G., Fractionation Control Apparatus, U.S. Patent 2,456,398 (Dec. 14, 1948).

334. Grimaud, G., "Automatic Control of the Operation of Distilling and Rectifying Columns", Bull. Assoc. Chim., 54, 506-16 (1937).

335. Harbert, W. D., "Distillation Column Balance", Pet. Refiner, 29, 117-22 (1950).

336. Hartmann, W. O., and A. G. Braun, "Control of Distillation Columns", Chem. Eng. Tech., 23, 39-41 (1951).

337. Highert, H. C., "Automatic Continuous Laboratory Still", Chem. and Industry, 49, 783-6 (1949).

338. Hills, Jr., C. W., "Control of Continuous Fractionating Columns", Canada Chem. and Proc. Ind., 32, 536-40 (1948).

339. Kern, D. Q., Process Heat Transfer. New York: McGraw-Hill Book Co., Inc., 1950. Pp. 780-9.

340. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology. New York: The Interscience Encyclopedia, Inc., 1947. Vol. I, Pp. 264-7.

341. Kolling, H., and H. Tramm, "Controls for Batch and Continuous Fractionating Columns in Laboratory and Pilot Plant Operation", Chemie-Ing. Tech., 21, 9-14 (1949).

342. Lebouvier, M., Distilling Liquids, French Patent 822,530 (Dec. 31, 1950).

343. Nelson, E. F., Fractionation, U.S. Patent 2,388,931 (Nov. 13, 1945).

344. Nelson, W. L., Petroleum Refinery Engineering, Second Edition. New York: McGraw-Hill Book Co., 1941. Pp. 379-83.

345. New York Vocational and Practical Arts Assn., Instruments and Process Control. Albany: Delmar Publishers, Inc., 1945. Pp. 155-82.

346. Perard, M., "Control and Regulation of Distilling Columns", Chim. et Ind., 25, 286-90 (1931).

347. Puertas, R. P., "Instrumentation in Alcohol Distillation", Inter. Sugar Journal, 49, 157-8 (1947).

348. Raw, R., "The Control of Fractional Distillation by Means of Refractive Index Methods", J. Soc. Chem., 66, 451-3 (1947).

349. Robinson, C. S., and E. R. Gilliland, The Elements of Fractional Distillation, Third Edition. New York: McGraw-Hill Book Co., 1939. Pp. 75-6.

350. Robinson, C. S., and E. R. Gilliland, The Elements of Fractional Distillation, Fourth Edition. New York: McGraw-Hill Book Co., 1950. Pp. 472-6.

351. Ibid., Pp. 131-2.

352. Sotek, S., and J. Fidler, Apparatus for Rectifying Alcohol, Austrian Patent 151,650 (Nov. 25, 1937).

353. Stanley, C. P., Automatic Control for Distillation Column, U.S. Patent 2,504,464 (April 18, 1950).

354. Uitti, K. D., "Control Point Location and Its Effect on Fractionation-Column Operation", Pet. Proc., 5, 41-4 (1950).

355. _____, "The Effect of Control Point Location Upon Column Control", Pet. Refiner, 29, 130-4 (1950).

356. Universal Oil Products, Technique for Controlling Distillation, Br. Patent 594,286 (1947).

357. Wherry, T. C., and F. W., Crawford, "Continuous Analysis and Control of Process Stream Composition with Infrared Analyzers", Oil Gas J., 48, 272-4 (1950).

Compilation of Equilibrium Data for the System Ethanol-Water at Atmospheric Pressure

358. Brown, G. G., and Assoc., Unit Operations. New York: John Wiley and Sons, Inc., 1951. Pp. 582.

359. Carey, J. S., and W. K. Lewis, "Studies in Distillation", Ind. Eng. Chem., 24, 882-3 (1932).

360. Cornell, L. W., and R. E. Montonna, "Studies in Distillation", Ind. Eng. Chem., 25, 1331-5 (1933).

361. Elliot, C., Distillation in Practice, First Edition. London: E. Benn Limited, 1925. Pp. 133.

362. Evans, P. N., "Boiling and Condensing Points of Alcohol-Water Mixtures", Ind. Eng. Chem., 8, 260-2 (1916).

363. Hausbrand, E., Principles and Practice of Industrial Distillation, Fourth Edition. London: Chapman and Hall Limited, 1925. Pp. 168.

364. Ibid., Pp. 283.

365. Horsley, L. H., et. al., Azeotropic Data. Washington: American Chemical Society, 1952. Pp. 6.

366. Noyes, W. A., and R. R. Warfel, "The Boiling-Point Curve for Mixtures of Ethyl Alcohol and Water", J. Am. Chem. Soc., 23, 463 (1901).

367. Othmer, D. F., "Composition of Vapors from Boiling Binary Solutions", Ind. Eng. Chem., 20, 743-7 (1928).

368. Perry, J. H., Chemical Engineers Handbook, Third Edition. New York: McGraw-Hill Book Co., Inc., 1950. Pp. 574.

369. Rayleigh, L., "Distillation of Binary Mixtures", Phil. Mag., 4, 521-37 (1902).

370. Robinson, C. S., and E. R. Gilliland, Elements of Fractional Distillation, Fourth Edition. New York: McGraw-Hill Book Co., Inc., 1950. Pp. 52.

371. Rosanoff, M. A., C. W. Bacon, and R. M. White, "A Rapid Laboratory Method of Measuring the Partial Vapor Pressures of Liquid Mixtures", J. Am. Chem. Soc., 36, 1803-25 (1914).

372. U.S. Bureau of Standards, Circular No. 19, 1924. Pp. 16-7.

373. Wade, J., and R. W. Merriam, "Influence of Water on the Boiling Point of Ethyl Alcohol at Pressures Above and Below the Atmospheric Pressure", J. Chem. Soc., 99, 997-1011 (1911).

374. Woodman, A. G., Food Analysis, Third Edition. New York: McGraw-Hill Book Co., Inc., 1931. Pp. 454-67.

375. Young, S., and E. C. Fortey, "The Properties of Mixtures of the Lower Alcohols with Water", J. Chem. Soc., 81, 719-23 (1902).

APPENDIX

TABLE I

EFFECT OF FUSEL OIL ON THE DETERMINATION OF ALCOHOL BY PICNOMETER, IMMERSION REFRACTOMETER AND HYDROMETER

Analytical Results in Degrees Proof at 60°F

Fusel Oil, Mg per 100 ml of sample	Analytical Method	Actual Alcohol Content at Which Samples were Prepared, Degrees Proof at 60°F								
		20°P	40°P	60°P	80°P	100°P	120°P	140°P	160°P	180°P
200	Picnometer	20.4	40.1	59.8	79.9	100.1	119.9	140.0	160.1	180.2
	Hydrometer	20.2	40.0	59.2	80.0	99.9	120.0	140.1	160.4	180.4
	Refractometer	20.4	40.2	59.4	79.6	-	-	-	-	-
500	Picnometer	20.7	40.6	60.8	80.8	100.8	120.9	140.8	160.4	180.8
	Hydrometer	20.6	40.4	60.2	80.6	100.4	120.8	140.8	160.9	180.4
	Refractometer	21.3	41.2	60.5	80.4	-	-	-	-	-
1000	Picnometer	21.5	41.7	62.0	82.2	102.2	122.1	142.1	162.2	182.1
	Hydrometer	21.8	41.6	61.8	82.4	102.4	122.3	142.4	162.6	182.6
	Refractometer	23.1	42.8	62.1	82.1	-	-	-	-	-
2000	Picnometer	23.3	43.8	64.4	84.5	104.6	124.4	144.4	164.1	184.0
	Hydrometer	23.6	43.8	64.9	84.1	104.8	124.6	144.3	164.4	184.2
	Refractometer	26.7	45.9	65.0	84.4	-	-	-	-	-
4000	Picnometer	i[1]	48.4	-	89.8	109.6	128.9	148.7	168.5	188.0
	Hydrometer	i	47.8	-	89.2	109.4	129.1	149.0	168.7	188.4
	Refractometer	i	51.4	-	92.0	-	-	-	-	-

[1] Two liquid layers formed.

(Continued on next page)

TABLE I (Continued)

Fusel Oil, Mg per 100 ml of sample	Analytical Method	Actual Alcohol Content at Which Samples were Prepared, Degrees Proof at 60°F								
		20°P	40°P	60°P	80°P	100°P	120°P	140°P	160°P	180°P
7000	Picnometer	i	i	77.4	97.2	116.2	135.7	155.2	174.6	-
	Hydrometer	i	i	77.2	97.0	115.9	135.3	155.7	174.4	-
	Refractometer	i	i	78.9	-	-	-	-	-	-
10,000	Picnometer	i	i	85.4	104.5	123.3	142.4	161.5	181.0	-
	Hydrometer	i	i	84.8	104.1	123.1	142.4	161.7	181.5	-
	Refractometer	i	i	88.4	-	-	-	-	-	-
15,000	Picnometer	i	i	97.7	115.9	134.3	153.3	172.1	190.6	-
	Hydrometer	i	i	97.2	115.3	134.3	153.8	172.2	190.8	-
	Refractometer	i	i	-	-	-	-	-	-	-
20,000	Picnometer	i	i	109.0	126.5	144.8	163.1	181.7	-	-
	Hydrometer	i	i	108.6	126.4	144.8	163.2	182.0	-	-
	Refractometer	i	i	-	-	-	-	-	-	-
30,000	Picnometer	i	i	129.7	146.7	164.3	182.6	-	-	-
	Hydrometer	i	i	129.6	146.9	164.6	182.7	-	-	-
	Refractometer	i	i	-	-	-	-	-	-	-

TABLE II

ALCOHOLIC CONTENT OF LIQUID PHASE BY PLATES
OF THE RECTIFYING COLUMN UTILIZING QUANTITY CONTROL
SYSTEM II

Experimental Conditions: Feed - 60°P at Plate 16;
Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.
50	189.6	191.7	191.7	191.4	191.2	190.7	190.0	190.5
46	184.3	189.7	190.5	190.5	189.3	189.2	188.7	188.2
42	187.9	188.4	187.7	187.9	185.2	184.5	183.0	182.1
40	186.2	187.2	186.4	186.3	183.4	182.0	180.1	177.9
38	184.9	185.7	183.8	184.4	180.0	176.5	173.6	171.1
36	183.6	183.7	181.0	180.8	174.1	170.4	162.0	157.4
34	181.7	180.3	176.9	172.6	164.8	158.8	139.2	131.1
32	178.3	175.8	170.3	165.2	148.2	131.1	57.4	53.6
30	171.9	168.5	156.0	146.8	103.9	50.0	20.3	19.7
28	162.0	154.3	118.2	99.0	33.8	18.0	13.5	13.3
26	129.0	110.0	43.4	30.4	16.5	12.2	12.1	11.2
24	35.3	35.9	15.8	14.3	11.0	10.8	11.3	11.0
22	15.0	16.7	13.2	12.6	10.6	11.0	11.8	10.6
20	10.8	12.7	12.1	11.9	10.6	11.3	11.4	10.6
18	10.0	11.4	11.6	12.1	9.9	11.3	11.3	10.6
14	4.9	5.3	5.5	4.9	4.6	4.7	6.0	5.4
12	0.3	5.1	0.7	0.5	0.4	0.2	0.5	0.7
10	0.3	0.2	0.0	0.0	0.2	0.0	0.0	0.0
8	0.4	0.0	0.0	0.1	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE III

FUSEL OIL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING QUANTITY CONTROL SYSTEM II

Experimental Conditions: Feed - 60°P at Plate 16; Reflux Ratio - 5:1; Product - Plate 42

Mgs. of Fusel Oil as Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.
50	15	35	10	20	25	25	30	30
46	20	5	25	20	35	50	60	70
42	20	70	50	120	210	240	380	460
40	50	90	110	140	360	480	700	500
38	80	100	220	260	800	900	1700	1600
36	120	230	460	600	1400	1800	3500	3000
34	180	360	1100	1500	2800	2800	3600	3600
32	290	800	1400	2400	3600	3600	1300	500
30	600	650	2600	3200	3600	550	210	250
28	1100	1700	2000	2800	600	200	80	80
26	1500	1400	700	400	100	70	30	50
24	280	320	100	60	40	20	15	25
22	35	70	30	25	15	10	10	15
20	20	25	10	15	5	5	10	10
18	10	15	5	10	10	15	15	10
14	5	5	5	5	5	5	10	5
12	5	5	5	5	5	5	5	5
10	10	5	5	5	5	5	5	5
8	10	5	5	5	5	5	5	20
6	10	5	5	5	10	5	5	5

TABLE IV

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM II[1]

Experimental Conditions: Feed - 60°P at Plate 16; Reflux Ratio - 5:1; Product - Overhead Distillate

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced					
	0 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.
50	191.2	191.7	191.6	191.4	191.7	191.1
42	188.0	187.4	185.1	186.8	185.3	187.5
36	182.6	181.0	171.8	182.0	176.3	181.8
30	150.6	148.3	135.8	147.2	140.0	148.3
24	35.9	38.0	28.6	36.2	34.1	35.0
20	14.2	12.1	10.9	10.9	14.5	16.3
18	12.0	10.8	10.6	8.9	13.3	10.2
14	7.3	6.5	4.0	5.0	4.5	4.1
10	0.3	0.2	0.0	0.3	0.2	0.2
6	0.0	0.0	0.0	0.0	0.0	0.0

[1] Based on varying the reflux ratio to maintain constant a reference temperature in the column.

TABLE V

TEMPERATURE OF VAPOR PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM II[1]

Experimental Conditions: Feed - 60°P at Plate 16; Reflux Ratio - 5:1; Product - Overhead Distillate

Temperature, Degrees Farenheit

Plate	Time of Reading After Withdrawal of Product Commenced					
	0 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.
50	172.5	172.5	172.5	172.5	172.5	172.5
42	175.0	175.5	175.5	173.0	176.0	175.0
34	176.5	177.0	177.5	177.0	178.0	177.0
30	180.0	181.0	183.5	181.0	184.0	181.5
26	191.0	192.0	192.5	192.0	193.5	193.0
22	199.0	203.0	205.0	202.0	203.0	202.5
18	203.0	203.5	203.0	203.0	204.5	203.5
16	205.0	205.5	205.0	205.5	206.0	205.0
12	215.0	215.5	215.5	215.5	217.0	216.0
6	219.0	219.5	219.0	219.0	219.5	219.0

[1] Based on varying the reflux rate to maintain constant a reference temperature in the column.

TABLE VI

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IIA[1]

Experimental Conditions: Feed - 60°P at Plate 16; Reflux Ratio - 5:1; Product - Overhead Distillate

Appatent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced					
	0 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.
50	191.7	191.5	191.8	191.6	191.7	191.6
42	189.2	188.8	189.6	188.6	188.2	188.8
36	183.9	183.6	184.4	184.1	183.6	183.5
30	153.2	152.2	154.0	153.7	153.8	152.5
24	40.2	38.7	41.6	40.9	39.6	39.0
20	17.3	16.1	17.0	17.4	16.1	16.6
18	14.0	13.1	14.5	14.9	13.6	13.9
14	8.3	7.0	8.6	7.6	8.3	7.2
10	0.4	0.3	0.2	0.3	0.0	0.4
6	0.0	0.0	0.0	0.0	0.0	0.0

[1] Based on varying the overhead product rate to maintain constant a reference temperature in the column.

TABLE VII

TEMPERATURE OF VAPOR PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IIA[1]

Experimental Conditions: Feed - 60°P at Plate 16; Reflux Ratio - 5:1; Product - Overhead Distillate

Temperature, Degrees Farenheit

Plate	Time of Reading After Withdrawal of Product Commenced					
	0 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs
50	172.5	172.5	172.5	172.5	172.5	172.5
42	174.5	173.0	175.0	173.5	175.0	175.0
34	176.5	176.5	177.0	177.0	176.5	176.5
30	179.5	180.0	180.0	180.0	180.0	180.0
26	190.5	191.0	191.5	191.5	191.0	191.0
22	198.0	198.0	198.5	198.5	198.5	198.5
18	200.5	200.5	201.0	200.5	200.5	200.5
16	203.0	203.5	203.0	203.0	203.5	203.0
12	215.0	215.5	215.5	215.5	215.5	215.5
6	219.0	219.0	219.0	219.5	219.0	219.0

[1] Based on varying the overhead product rate to maintain constant a reference temperature in the column.

TABLE VIII

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM III[1]

Experimental Conditions: Feed - 60°P at Plate 17; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced				
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.
50	191.8	192.6	191.9	192.2	191.7
42	189.6	190.7	190.6	190.3	190.1
38	188.3	189.0	188.5	188.6	188.5
34	185.7	186.7	185.8	186.1	185.9
30	182.8	183.4	182.0	182.1	181.5
26	175.4	177.1	174.4	174.9	174.0
24	168.8	171.1	163.3	169.6	169.3
23	164.5	166.6	168.5	165.9	164.1
22	158.7	161.2	159.8	161.7	160.4
21	151.4	154.8	151.4	155.8	152.8
20	143.3	145.9	141.1	149.8	145.8
19	121.3	121.3	118.1	136.6	131.1
17	44.0	45.3	47.1	67.6	65.8
16	24.4	22.0	24.0	43.6	37.8
15	10.3	9.2	9.4	19.6	12.6
14	7.2	4.6	5.8	11.1	8.1
12	---	0.5	0.7	4.2	3.0
10	---	0.4	0.5	0.5	0.7
8	---	0.2	0.0	0.7	0.3
4	0.5	0.2	0.0	0.2	0.3

[1] Based on varying the rate of withdrawal of the product as a side stream to maintain constant a reference temperature in the column.

TABLE IX

FUSEL OIL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM III[1]

Experimental Conditions: Feed - 60°P at Plate 17; Reflux Ratio - 5:1; Product - Plate 42

Mgs. of Fusel Oil as Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced				
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.
50	15	10	15	20	25
42	15	15	25	30	25
38	25	35	55	65	65
34	65	95	165	350	300
30	200	320	700	650	850
26	620	1,050	1,850	3,000	4,500
24	1,150	1,800	1,500	3,500	5,000
23	1,450	2,400	4,500	4,000	6,500
22	1,700	4,000	---	5,000	8,000
21	1,950	5,000	7,500	6,500	9,500
20	2,050	5,500	7,500	8,000	11,000
19	2,150	5,500	6,500	10,000	11,000
17	400	600	950	4,000	4,500
16	250	240	240	2,500	3,150
15	100	70	110	400	90
14	100	45	65	250	220
12	40	15	20	100	55
10	20	10	15	50	25
8	10	5	10	15	15
4	5	5	10	10	10

[1] Based on varying the rate of withdrawal of the main product as a side stream to maintain constant a reference temperature in the column.

TABLE X

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM III[1]

Experimental Conditions: Feed - 60°P at Plate 17;
Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced						
	4 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	191.7	192.9	192.6	192.6	192.4	192.9	192.9
42	190.7	190.7	190.7	190.5	190.5	191.0	190.7
38	189.0	189.0	188.9	188.7	188.8	188.8	188.9
34	187.0	187.0	186.4	186.2	186.1	186.1	186.2
30	183.9	183.9	183.2	183.1	181.9	182.5	182.5
26	177.1	178.5	177.4	177.1	176.5	176.3	176.4
24	172.5	173.5	172.9	173.5	173.3	171.4	171.8
23	169.4	171.5	170.3	170.1	169.8	167.5	168.6
22	165.0	169.4	166.9	167.0	166.8	164.3	165.2
21	159.2	161.7	161.0	161.3	161.2	158.6	160.4
20	152.9	157.9	156.9	156.1	156.9	154.6	156.5
19	137.3	145.8	146.3	147.0	148.4	144.9	148.5
17	67.2	79.5	83.8	87.1	89.4	82.3	88.1
16	43.7	63.5	73.5	79.5	87.6	77.0	88.2
14	9.2	20.7	27.9	13.2	55.3	47.3	62.2
12	1.5	4.8	7.8	10.1	19.1	18.2	16.1
8	0.5	0.2	0.2	0.0	0.2	0.4	0.6

[1] Based on varying the rate of withdrawal of the Main Product as a side stream to maintain constant a reference temperature in the column.

TABLE XI

FUSEL OIL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM III[1]

Experimental Conditions: Feed - 60°P at Plate 17; Reflux Ratio - 5:1; Product - Plate 42

Mgs. of Fusel Oil as Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced						
	4 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	20	20	25	25	25	25	10
42	25	25	35	30	35	35	40
38	40	45	65	60	60	70	85
34	160	160	200	240	240	280	220
30	360	360	480	600	600	740	700
26	1,200	1,100	1,450	1,650	1,800	2,200	2,000
24	2,000	2,000	2,350	2,550	2,650	3,100	3,000
23	2,550	2,350	2,650	---	2,250	4,500	3,750
22	2,950	2,650	3,200	3,000	3,500	6,750	6,250
21	3,750	3,300	4,750	4,750	4,500	8,250	8,500
20	4,500	4,000	5,750	5,050	5,500	9,350	9,000
19	4,750	5,250	6,250	6,500	7,000	9,500	10,500
17	1,600	2,200	2,650	3,200	3,200	4,750	5,250
16	800	1,700	2,500	2,950	3,750	4,750	5,750
14	110	380	640	980	2,650	2,300	4,000
12	30	95	160	280	660	700	750
8	15	20	30	30	50	60	55

[1] Based on varying the rate of withdrawal of the main product as a side stream to maintain constant a reference temperature in the column.

TABLE XII

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IV[1]

Experimental Conditions: Feed - 80°P at Plate 18;
Reflux Ratio - 4:1; Product - Plate 42

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced						
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	192.2	192.1	191.9	191.9	192.1	191.9	191.6
42	189.6	189.0	189.0	189.5	189.3	189.5	189.6
38	187.0	186.8	186.5	186.8	186.7	186.3	186.0
34	184.2	183.2	183.0	183.8	183.3	183.1	183.0
30	179.7	178.3	178.0	177.9	177.2	177.6	178.4
26	171.1	169.1	168.6	168.5	167.3	167.2	168.7
24	160.9	160.4	160.1	160.9	159.8	158.7	160.3
23	155.7	154.4	153.5	154.1	153.1	153.6	153.9
22	150.8	147.0	147.0	147.8	147.0	146.9	146.6
21	133.1	132.8	133.8	133.8	135.2	134.6	135.5
20	118.5	114.8	115.8	119.7	119.5	123.2	122.5
19	75.6	74.5	77.2	83.7	82.5	87.5	83.8
18	44.6	44.1	44.4	50.8	52.6	44.7	51.9
17	20.7	24.5	16.4	29.8	24.1	28.1	25.7
16	9.2	9.5	7.1	7.4	9.2	10.7	8.1
15	3.7	4.9	3.3	4.2	3.0	3.5	2.6
14	0.8	2.1	0.9	0.7	1.0	2.5	1.8
12	0.6	0.8	0.0	0.4	0.0	0.1	0.9
8	0.4	0.0	0.0	0.2	0.0	0.0	0.0
4	0.2	0.0	0.5	0.0	0.0	0.0	0.0

[1] Based on varying the feed rate to maintain constant a reference temperature in the column.

TABLE XIII

FUSEL OIL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IV[1]

Experimental Conditions: Feed - 80°P at Plate 18;
Reflux Ratio - 4:1; Product - Plate 42

Mgs. Fusel Oil as Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced						
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	10	5	0	10	10	10	---
42	15	25	30	25	40	40	30
38	65	100	125	110	130	135	125
34	185	325	200	395	260	215	160
30	580	1,200	1,200	1,150	1,350	1,400	1,400
26	2,000	3,100	3,400	3,700	3,750	4,650	4,450
24	3,650	4,800	6,100	6,400	6,550	5,850	6,600
23	3,950	6,950	7,550	8,250	8,900	8,800	8,450
22	5,350	7,100	9,000	9,500	9,350	8,850	8,800
21	5,800	8,100	9,100	9,850	10,400	11,500	10,600
20	5,500	6,750	8,300	9,800	10,300	--	10,400
19	1,950	2,950	2,950	4,850	4,250	5,550	4,800
18	630	600	750	800	1,050	1,250	900
17	290	405	605	625	760	760	550
16	70	105	130	120	170	170	140
15	30	50	75	75	65	70	70
14	15	50	30	45	25	60	45
12	15	25	5	40	5	10	25
8	35	25	20	35	0	30	45
4	25	30	40	45	0	40	45

[1] Based on varying the feed rate to maintain constant a reference temperature in the column.

TABLE XIV

ALCOHOL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IV[1]

Experimental Conditions: Feed - 80°P at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content in Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced						
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	191.3	191.4	191.1	190.7	191.3	191.1	191.3
42	187.7	187.7	187.7	187.7	187.9	187.7	188.0
38	183.8	183.3	182.7	183.0	183.3	183.6	183.5
34	178.8	177.5	177.8	177.4	177.8	178.4	178.4
30	171.0	168.9	169.5	169.5	169.5	169.5	170.0
26	157.4	156.9	156.3	156.3	156.0	156.3	157.4
24	148.1	146.0	147.5	145.0	146.5	146.9	148.3
23	142.9	139.7	141.3	139.7	140.4	140.7	141.8
22	136.0	135.1	136.0	135.7	136.0	136.3	135.6
21	122.5	121.9	125.0	125.1	124.8	125.1	125.3
20	106.8	108.5	113.5	115.1	114.9	115.1	114.9
19	83.8	84.7	88.7	88.5	89.3	89.5	88.5
18	56.9	60.2	60.1	60.8	60.3	60.1	59.0
17	27.4	30.0	30.6	30.4	30.0	31.0	31.0
16	12.7	15.6	14.0	15.1	15.4	16.0	16.0
15	5.8	4.5	5.7	4.1	5.0	5.8	5.5
14	1.8	2.5	2.7	2.5	2.5	2.6	2.5
12	0.4	0.3	0.4	0.4	0.4	0.4	0.4
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[1] Based on varying the feed rate to maintain constant a reference temperature in the column.

TABLE XV

FUSEL OIL CONTENT OF LIQUID PHASE BY PLATES OF THE RECTIFYING COLUMN UTILIZING COMPOSITION CONTROL SYSTEM IV[1]

Experimental Conditions: Feed - 80°P at Plate 18;
Reflux Ratio - 3:1; Product - Plate 42

Mgs. Fusel Oil as Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced						
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	24 hrs.
50	15	15	10	10	10	10	15
42	50	95	80	85	85	80	80
38	400	600	550	600	500	450	500
34	800	1,250	1,300	1,550	1,400	1,100	1,350
30	2,000	3,500	3,600	5,550	3,800	3,800	3,650
26	5,500	8,500	8,600	9,800	9,000	8,500	8,100
24	8,500	10,500	12,300	13,600	13,500	12,100	11,400
23	8,500	11,300	13,500	15,500	14,800	13,300	12,900
22	8,500	12,000	14,200	16,100	15,000	14,900	14,500
21	8,500	11,200	13,800	15,500	---	14,600	14,300
20	7,500	9,000	13,100	14,100	13,200	13,500	13,100
19	2,000	3,500	5,900	5,400	6,300	5,700	5,250
18	950	1,000	1,600	2,350	2,350	1,800	1,650
17	200	600	800	1,000	1,000	1,000	1,100
16	120	180	330	370	460	440	380
15	50	75	50	100	100	100	100
14	20	40	50	55	90	75	70
12	5	5	15	15	20	15	15
8	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0

[1] Based on varying the feed rate to maintain constant a reference temperature in the column.

TABLE XVI

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	15	20	15	10	15	20	20	20	25
42	20	25	25	30	40	40	50	50	55
38	35	55	65	115	250	150	250	250	250
34	90	170	250	450	550	500	800	700	750
30	500	700	800	1,600	2,500	2,000	3,000	3,000	3,500
26	2,000	3,000	4,000	5,500	6,000	6,000	7,500	9,000	7,500
24	3,000	5,000	6,500	10,000	11,000	11,500	14,000	13,000	12,500
23	4,000	6,000	8,000	11,000	13,500	14,000	14,000	16,500	14,000
22	4,500	7,000	10,000	13,500	14,500	16,000	17,000	17,500	17,000
21	5,500	8,500	11,500	13,500	16,000	17,000	18,500	18,500	17,500
20	5,000	8,000	11,000	13,500	16,000	16,500	15,000	16,000	16,000
19	1,200	3,000	4,000	5,000	7,500	---	5,000	6,000	5,500
18	500	600	950	1,100	1,500	2,500	1,500	2,000	1,500
17	350	350	550	650	800	1,300	700	750	600
16	65	110	200	250	350	500	300	350	300
15	40	55	95	120	200	300	150	200	150
14	25	40	65	85	100	140	100	110	90
12	15	20	30	50	50	70	50	60	50
8	5	10	15	20	20	25	15	20	15
4	0	10	5	5	5	10	5	10	5

Feed to Rectifying Column - 75
Product from Rectifying Column - 45
Heads from Rectifying Column - 20

TABLE XVII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	190.9	192.5	192.4	192.0	191.1	192.1	192.0	191.8	192.5
42	190.2	190.3	190.1	192.0	189.2	190.0	189.5	189.6	189.9
38	188.5	188.2	188.1	188.0	187.0	187.7	186.7	187.2	187.0
34	185.8	185.6	185.4	184.2	183.6	185.6	182.9	183.4	183.4
30	181.7	181.6	181.0	178.1	177.2	178.7	176.3	177.6	176.6
26	174.3	172.9	172.2	167.0	166.1	167.7	163.6	164.4	164.5
24	166.6	164.3	163.8	156.7	156.0	157.4	152.6	154.2	154.0
23	159.7	157.9	157.6	148.5	148.5	150.1	144.6	145.6	146.8
22	150.9	150.6	144.5	139.0	139.5	143.5	137.2	138.9	138.9
21	131.5	135.1	137.1	126.5	132.0	135.1	124.6	124.1	125.2
20	108.4	114.7	119.3	110.7	118.7	125.5	108.0	108.9	108.8
19	52.8	57.4	61.8	56.9	62.0	61.5	53.2	56.5	54.7
18	28.5	31.7	34.4	30.8	34.1	32.0	30.2	29.4	28.1
17	17.1	19.3	21.1	18.5	22.9	21.6	20.5	17.1	16.5
16	7.8	9.4	10.4	9.4	12.3	10.2	10.3	8.7	8.0
15	3.9	4.5	4.5	4.7	5.7	5.1	3.6	4.2	3.9
14	1.6	2.2	2.6	2.0	3.2	2.2	1.7	2.1	2.2
12	0.2	0.4	0.5	2.2	0.9	1.3	0.4	0.5	0.5
8	0.0	0.0	0.1	0.1	0.06	0.0	0.0	0.06	0.0
4	0.0	0.0	0.1	0.0	0.06	0.0	0.0	0.1	0.0

Feed to Rectifying Column - 39.4
Product from Rectifying Column- 189.9
Heads from Rectifying Column - 192.6

TABLE XVIII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	15	15	15	20	25	15	15	25	20
42	30	45	50	55	55	40	45	40	40
38	70	150	250	250	300	200	200	200	200
34	250	550	800	750	750	500	500	250	450
30	650	1,900	3,000	3,000	3,000	2,000	2,500	1,500	2,000
26	2,900	5,500	7,500	7,500	7,000	5,000	4,500	3,500	4,500
24	5,500	8,000	10,000	11,000	10,000	7,500	6,500	6,500	6,500
23	6,500	10,000	12,000	13,000	12,000	9,000	8,500	7,500	7,500
22	7,000	10,500	13,500	13,500	13,500	10,000	9,000	8,500	8,000
21	6,000	9,500	12,500	13,000	12,000	9,000	9,000	8,000	7,500
20	4,500	8,000	9,500	11,500	9,000	7,000	7,000	6,000	6,000
19	1,500	2,500	3,500	4,000	3,500	2,500	2,500	2,500	2,000
18	300	500	550	700	500	400	450	400	300
17	200	300	400	450	400	250	300	300	200
16	55	90	105	145	90	75	75	75	70
15	35	55	45	75	60	45	50	50	50
14	20	35	45	50	40	30	25	35	30
12	15	25	25	25	20	15	15	20	20
8	10	10	25	15	10	10	10	15	10
4	5	5	15	10	10	10	10	10	5

Feed to Rectifying Column - 50
Product from Rectifying Column - 45
Heads from Rectifying Column - 20

TABLE XIX

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.0	190.5	191.8	191.7	192.0	191.9	191.7	191.5	191.7
42	189.5	188.3	189.4	189.5	189.5	189.5	189.5	189.5	189.1
38	187.1	185.8	186.5	186.6	186.6	187.0	187.0	186.8	186.4
34	184.2	182.9	182.6	183.1	183.0	183.6	183.9	183.6	183.5
30	179.4	176.6	176.2	176.1	176.4	178.0	178.2	177.9	178.3
26	170.1	166.6	165.5	164.6	165.2	167.8	168.8	168.6	168.8
24	160.2	156.9	154.6	154.5	155.6	158.1	159.0	159.4	159.1
23	151.3	148.7	147.1	147.0	147.4	150.1	151.3	152.2	151.9
22	141.0	139.3	138.6	138.6	138.7	140.3	141.4	142.0	142.4
21	115.8	118.9	121.0	120.2	119.1	120.4	122.8	120.3	120.1
20	92.6	98.4	98.0	98.3	96.1	96.1	99.8	95.9	97.2
19	45.9	47.5	49.9	43.7	48.2	47.9	49.7	41.7	49.7
18	29.5	30.3	29.3	30.1	30.8	31.2	32.7	31.3	30.0
17	19.2	19.4	18.9	19.2	19.3	20.4	20.7	21.2	19.2
16	9.8	9.6	9.6	9.7	9.2	10.8	9.6	10.9	9.6
15	5.7	6.0	1.5	4.7	5.1	6.0	5.6	6.4	5.5
14	2.4	2.8	2.6	2.4	2.2	3.0	2.1	2.6	2.6
12	0.5	0.5	0.7	0.5	0.5	0.5	0.3	0.5	0.5
8	0.3	0.2	0.1	0.2	0.1	0.3	0.1	0.1	0.1
4	0.2	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0

Feed to Rectifying Column - 38.7
Product from Rectifying Column - 189.5
Heads from Rectifying Column - 191.3

TABLE XX

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	15	20	20	20	20	20	25	15	25
42	40	70	115	100	120	140	150	110	120
38	200	300	550	550	500	650	500	500	500
34	400	700	1,500	2,000	2,000	2,000	2,000	1,500	2,000
30	1,500	3,500	3,000	4,000	4,000	4,000	3,500	4,000	3,500
26	3,000	4,500	5,500	6,500	7,000	7,000	7,000	6,000	7,000
24	3,500	5,500	6,500	8,500	9,500	9,000	8,500	7,500	8,000
23	3,500	5,000	6,500	7,500	9,500	8,000	8,000	7,000	7,500
22	2,500	4,500	5,500	6,000	9,000	7,500	6,500	7,000	7,000
21	1,500	2,500	3,500	4,000	6,500	5,000	5,000	4,500	5,000
20	900	1,100	1,800	3,000	4,500	3,500	3,500	3,000	3,000
19	250	450	500	750	1,000	700	700	650	750
18	70	250	130	200	300	250	200	200	250
17	55	85	105	200	250	250	170	150	150
16	30	45	55	80	95	80	80	80	75
15	20	30	35	50	55	55	45	50	60
14	5	20	25	35	40	35	25	40	35
12	5	15	15	20	35	25	15	25	
8	0	10	10	15	20	15	10	15	30
4	0	0	5	5	10	10	5	5	5

Feed to Rectifying Column - 70
Product from Rectifying Column - 120 Av.
Heads from Rectifying Column - 20

TABLE XXI

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	189.8	191.0	190.8	191.2	191.0	191.0	190.7	189.8	191.2
42	187.5	187.5	187.2	188.7	187.4	187.1	186.9	186.9	186.9
38	183.9	183.4	182.5	182.5	182.5	182.7	182.8	183.0	182.2
34	179.5	178.0	176.5	176.0	177.5	176.7	176.2	176.8	176.2
30	172.8	170.8	168.5	167.5	169.1	167.3	167.6	168.2	167.9
26	160.2	157.7	154.3	153.2	156.1	154.1	143.4	153.6	153.2
24	145.5	141.6	138.1	138.9	143.4	145.3	138.6	139.8	138.6
23	130.5	126.0	121.4	125.2	133.4	128.7	125.6	127.4	125.1
22	114.2	111.2	107.5	111.4	121.0	115.1	111.6	113.0	112.0
21	84.1	85.2	79.5	85.3	96.5	87.6	89.6	87.6	86.4
20	65.5	68.4	65.6	67.0	75.8	70.8	72.8	68.7	69.6
19	43.0	43.3	42.2	43.7	45.1	44.1	43.8	42.9	43.8
18	34.4	34.9	32.4	33.9	33.9	35.4	34.3	33.9	34.7
17	26.6	26.3	26.0	26.7	25.9	26.9	27.7	26.8	27.1
16	17.8	22.2	16.4	17.7	15.9	17.7	19.1	17.7	20.4
15	11.7	11.5	10.1	10.6	9.3	11.0	11.5	10.9	11.0
14	6.9	6.5	6.0	7.2	5.5	6.2	6.9	7.6	7.8
12	1.8	2.2	1.8	2.2	2.0	2.3	2.6	2.5	3.3
8	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 38.6
Product from Rectifying Column - 186.6
Heads from Rectifying Column - 191.3

TABLE XXII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	110	200	200	100	200	200	150	65	70
46	500	450	450	500	400	450	400	350	300
42	1,350	1,500	1,100	1,500	1,300	2,000	1,500	1,100	950
40	2,000	2,000	2,500	2,000	2,000	2,000	2,000	2,000	2,000
38	3,500	2,500	2,500	2,000	2,500	2,000	2,000	2,000	2,500
36	3,000	2,000	2,500	2,000	2,000	2,000	1,500	2,000	2,500
34	2,500	2,000	2,500	2,000	2,000	2,000	1,500	1,500	2,000
32	2,500	2,000	2,000	2,000	2,000	2,000	1,500	1,500	1,500
30	2,000	2,000	2,000	2,000	2,000	2,000	1,000	950	1,200
28	2,000	2,000	1,500	2,000	1,500	2,000	1,000	800	1,150
26	1,650	1,500	1,050	900	1,500	1,050	350	600	1,050
24	1,450	1,500	850	850	1,500	850	200	450	900
22	1,250	700	750	850	1,500	850	150	300	650
20	900	400	550	550	1,000	550	100	135	500
18	95	80	200	200	90	85	70	70	80
16	55	50	100	100	55	50	40	40	45
14	30	30	25	30	30	30	20	20	20
10	15	15	15	20	15	15	5	10	10
6	10	10	15	15	15	10	5	5	10
2	5	10	10	5	10	5	5	5	5

Feed to Rectifying Column - 85
Product from Rectifying Column - 450
Heads from Rectifying Column - 45

TABLE XXIII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 20% Alcohol in Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	185.8	183.7	184.4	183.8	184.9	185.4	184.2	184.3	185.6
46	180.0	178.1	177.8	178.4	179.3	178.7	177.9	179.9	181.2
42	168.3	167.1	166.2	166.0	165.5	167.3	164.6	166.0	169.0
40	159.1	158.2	157.3	156.4	156.1	157.3	153.9	155.8	161.9
38	150.2	150.7	148.1	148.5	143.6	146.6	144.5	141.4	152.6
36	132.9	134.0	130.5	130.5	122.7	128.6	126.1	119.4	136.4
34	128.0	131.0	127.1	127.1	119.0	125.7	122.4	114.0	121.6
32	116.9	113.8	110.3	111.3	99.6	108.6	102.5	95.3	103.7
30	110.3	107.8	104.8	104.1	96.6	102.5	100.2	95.7	104.1
28	106.6	102.3	98.4	98.4	91.0	95.2	89.6	88.2	99.0
26	101.9	93.7	93.5	94.3	87.1	91.9	---	76.2	92.2
24	93.2	84.2	84.6	86.0	80.6	82.1	---	69.7	83.3
22	88.7	77.4	81.5	81.5	77.6	79.8	---	58.0	71.8
20	71.2	61.1	65.9	66.8	66.8	62.2	---	47.8	56.3
18	39.5	40.2	38.7	39.9	45.1	39.6	40.0	39.7	39.4
16	30.8	33.2	32.0	32.5	31.9	30.9	33.4	33.5	32.7
14	21.8	21.4	19.5	20.8	19.6	19.4	21.3	24.9	20.4
10	2.3	3.6	4.4	4.3	3.4	3.0	3.9	6.9	4.0
6	0.06	0.08	1.3	1.0	0.5	0.2	0.4	0.7	0.4
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 36.6
Product from Rectifying Column - 178.8
Heads from Rectifying Column - 185.8

TABLE XXIV

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio - 15:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.
50	5	5	5	5	5	5	5	5
42	5	5	5	5	5	5	5	5
38	10	10	10	10	15	10	10	10
34	20	30	35	30	45	35	40	50
30	85	115	165	150	235	150	190	260
26	525	740	930	650	950	750	800	1,050
24	1,100	1,550	1,850	1,900	2,600	2,450	2,650	2,850
23	2,150	2,650	2,950	3,300	5,000	3,650	4,000	4,100
22	3,400	3,550	4,400	4,900	7,100	5,650	5,550	5,800
21	4,600	5,750	6,900	7,800	8,500	8,200	9,000	8,500
20	5,500	6,450	7,900	9,300	10,750	10,400	10,700	10,500
19	4,400	5,300	6,650	6,750	7,100	—	7,500	7,700
18	1,750	550	700	1,400	1,150	2,900	2,950	2,000
17	255	180	345	460	510	570	605	655
16	40	20	20	95	95	95	165	150
15	15	10	55	35	30	25	45	40
14	5	5	5	15	10	5	15	15
12	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 85
Product from Rectifying Column - 5
Heads from Rectifying Column - 5

TABLE XXV

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions:. Feed - 30% Alcohol at Plate 18; Reflux Ratio - 15:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.
50	192.6	192.4	192.2	192.9	192.8	192.9	192.8	192.8
42	191.3	190.6	190.8	191.0	190.9	191.0	191.1	191.0
38	190.4	190.2	190.4	190.0	190.1	190.2	190.0	190.1
34	188.9	188.9	188.9	188.7	188.8	188.7	188.9	188.8
30	187.0	185.9	186.2	186.4	186.2	186.4	186.5	186.6
26	182.3	180.8	180.6	181.2	181.6	181.1	181.0	181.6
24	176.4	174.8	174.8	175.0	175.6	175.1	175.2	175.8
23	170.9	170.3	170.1	170.8	170.9	170.7	170.7	170.6
22	163.0	163.3	163.0	163.3	164.2	163.6	163.3	163.0
21	147.8	145.8	147.9	148.4	149.5	148.5	147.4	147.8
20	129.7	132.8	133.0	133.5	134.2	134.0	133.6	133.0
19	85.1	88.0	88.6	89.2	89.6	88.5	87.9	88.2
18	--	40.9	36.6	35.2	35.4	39.5	42.3	39.7
17	17.4	13.7	14.7	13.2	16.3	16.3	14.8	15.9
16	3.0	2.0	2.2	2.8	2.8	4.4	3.4	3.8
15	0.7	0.2	0.7	0.8	0.5	0.4	0.9	0.7
14	0.0	0.0	0.3	0.2	0.4	0.3	0.5	0.6
12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 58.8
Product from Rectifying Column - 191.7
Heads from Rectifying Column - 192.9

TABLE XXVI

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio 10:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	5	5	5	5	--	15	10
42	5	5	5	10	10	10	10	10
38	20	15	20	20	20	30	20	20
34	30	40	55	60	100	60	70	60
30	100	180	310	330	480	260	280	300
26	590	700	1,100	1,400	2,200	1,150	1,100	1,600
24	1,150	1,600	2,500	3,100	3,950	2,550	3,050	3,100
23	1,680	2,500	3,600	4,500	6,000	3,900	4,300	3,900
22	2,400	3,800	4,800	5,700	7,400	5,300	5,100	4,900
21	3,100	4,200	6,300	7,900	9,700	6,900	6,400	6,800
20	3,500	5,000	7,300	9,000	10,300	7,400	7,100	7,100
19	1,600	1,700	4,500	6,000	7,400	6,000	4,050	4,050
18	520	410	900	1,100	1,250	1,200	600	600
17	97	290	420	300	640	200	220	190
16	15	25	50	65	100	55	70	55
15	10	10	20	25	35	25	20	20
14	5	0	5	10	10	5	5	5
12	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 60
Product from Rectifying Column - 10
Heads from Rectifying Column - 5

TABLE XXVII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 30% Alcohol at Plate 18; Reflux Ratio - 10:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.2	192.0	192.2	192.1	192.1	192.3	192.2	192.2
42	191.1	191.2	191.2	191.1	191.0	191.3	191.1	191.1
38	190.0	190.3	190.0	190.0	189.9	190.1	189.9	190.2
34	187.9	188.1	187.6	187.7	187.9	188.0	188.0	187.9
30	185.3	185.8	185.4	185.4	185.3	185.6	185.6	185.6
26	179.5	179.6	179.4	179.4	179.1	179.7	179.3	179.3
24	174.2	174.2	173.9	173.6	173.6	174.0	176.3	173.6
23	168.9	169.3	168.9	168.8	169.4	168.7	168.2	169.0
22	161.4	161.6	161.8	161.8	161.9	161.7	161.7	162.0
21	149.1	149.3	148.5	149.1	148.5	149.4	149.6	149.2
20	125.7	127.4	127.0	130.4	131.0	130.9	127.3	128.3
19	71.4	69.2	91.5	76.9	79.0	76.4	75.7	74.1
18	34.6	37.1	35.8	39.7	35.6	39.1	34.9	34.5
17	17.0	16.2	15.2	14.6	17.7	15.1	14.6	14.5
16	2.8	3.2	3.7	2.6	5.3	3.3	4.3	3.4
15	0.7	0.3	0.7	0.9	0.9	0.9	0.7	0.8
14	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.2
12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 59.5
Product from Rectifying Column - 190.7
Heads from Rectifying Column - 192.4

TABLE XXVIII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	5	15	10	15	15	10	5	20
42	10	10	20	20	10	25	20	20	25
38	20	30	50	80	85	85	100	90	65
34	80	134	195	230	260	270	260	255	270
30	365	400	850	700	1,350	1,100	1,100	1,300	1,250
26	1,100	1,900	2,950	3,750	5,250	3,850	4,300	4,500	4,150
24	2,300	3,900	6,050	7,550	8,100	8,300	8,250	7,500	7,700
23	2,950	5,350	8,000	10,000	10,420	9,000	10,700	10,760	11,190
22	3,950	7,300	10,500	10,900	11,600	11,300	11,400	11,050	12,600
21	4,700	7,900	11,400	11,500	13,150	12,800	12,000	13,000	14,000
20	4,450	7,850	10,500	10,000	13,050	11,400	10,500	11,150	12,450
19	850	2,000	2,450	4,150	5,450	3,700	3,450	3,750	2,700
18	335	840	800	750	750	650	700	1,000	650
17	205	325	470	655	655	770	610	600	565
16	71	123	160	210	240	270	180	200	200
15	30	50	70	80	100	90	80	80	90
14	20	25	45	60	60	50	50	55	45
12	5	10	15	20	20	25	15	20	15
8	0	5	10	0	5	10	0	5	5
4	0	0	5	5	10	10	0	0	0

Feed to Rectifying Column - 80
Product from Rectifying Column - 20
Heads from Rectifying Column - 10

TABLE XXIX

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 30% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.2	192.4	192.0	192.0	192.0	192.0	192.2	192.2	191.4
42	189.8	190.2	190.0	189.6	189.8	189.8	190.0	190.1	189.9
38	188.1	188.0	187.5	188.0	187.6	187.6	187.6	187.6	187.3
34	—	185.3	184.7	184.8	184.6	184.8	184.8	184.6	184.5
30	181.6	181.2	179.7	179.9	179.4	179.6	179.4	179.8	179.7
26	174.3	173.7	171.1	170.5	169.5	170.1	169.3	170.5	170.5
24	167.3	165.6	162.7	162.0	160.7	160.2	159.9	161.4	160.6
23	160.0	159.8	156.5	155.8	154.3	154.1	153.8	154.7	154.7
22	153.5	151.6	148.5	148.3	146.6	146.9	145.6	147.2	147.5
21	136.7	137.8	132.6	132.6	133.0	135.6	132.7	132.4	133.6
20	117.1	118.5	110.3	116.4	118.3	118.9	114.4	114.3	115.9
19	54.3	56.5	60.1	70.7	69.6	63.6	65.5	64.6	60.2
18	37.4	42.3	40.0	35.5	36.5	38.3	37.4	41.6	37.3
17	22.3	20.6	21.4	24.8	19.8	25.0	21.4	22.0	19.1
16	9.6	8.3	10.9	11.7	8.3	11.5	8.3	9.4	7.4
15	0.9	2.4	8.3	3.6	2.2	3.0	2.4	3.3	0.9
14	0.4	—	—	1.8	1.1	1.3	1.2	1.6	0.7
12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 58.7
Product from Rectifying Column - 189.9
Heads from Rectifying Column - 192.7

TABLE XXX

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	10	15	30	20	20	25	30	25	25
42	20	25	45	45	50	50	50	--	40
38	55	70	110	200	250	200	--	200	200
34	150	250	400	600	750	500	550	550	500
30	500	850	1,400	2,500	2,500	4,000	2,500	2,500	2,000
26	1,400	2,500	4,000	5,000	5,000	4,500	5,000	5,000	4,500
24	2,500	4,000	6,500	8,000	8,500	7,000	7,500	7,500	7,000
23	4,000	5,000	8,000	9,000	10,500	9,000	9,500	9,000	7,000
22	4,000	7,000	9,000	9,500	11,500	10,500	10,000	10,000	8,000
21	4,000	7,500	9,000	10,000	12,500	13,000	12,000	10,500	9,000
20	3,500	6,500	8,000	10,000	11,500	13,000	11,500	10,000	9,000
19	1,000	3,500	3,500	4,500	6,000	6,000	11,500	5,000	3,500
18	300	600	1,400	1,200	1,300	1,400	2,000	2,000	1,500
17	200	450	700	650	900	1,050	1,050	800	600
16	100	160	300	350	400	400	450	500	300
15	40	85	100	115	165	200	250	200	150
14	25	55	80	85	110	150	150	150	80
12	10	25	35	35	50	60	55	55	35
8	5	10	15	10	15	15	20	15	10
4	0	5	--	10	5	5	10	10	5

Feed to Rectifying Column - 65
Product from Rectifying Column - 35
Heads from Rectifying Column - 20

TABLE XXXI

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 30% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.1	192.0	192.0	192.0	191.7	191.8	192.1	191.7	192.0
42	189.6	189.6	189.3	189.2	189.1	189.1	189.3	188.9	189.3
38	187.2	187.1	186.7	186.7	186.4	186.5	186.0	186.0	186.9
34	184.4	184.0	182.6	182.9	182.7	183.1	182.6	182.3	183.4
30	179.4	179.0	178.2	177.3	176.6	177.7	177.7	176.6	178.0
26	172.0	169.8	168.9	166.6	166.5	167.9	168.0	166.7	168.8
24	164.2	161.5	160.4	157.9	156.7	160.1	159.7	157.8	159.3
23	156.6	156.2	153.4	151.5	151.2	151.2	153.4	152.2	152.1
22	148.2	149.1	146.2	144.2	141.9	144.8	146.9	144.8	145.5
21	128.3	133.4	135.1	131.9	131.4	133.3	133.6	131.6	134.9
20	113.3	114.2	115.8	116.9	114.8	118.1	119.2	114.0	119.1
19	64.2	72.9	73.7	73.5	76.8	77.2	77.9	71.4	72.1
18	42.8	42.2	44.0	45.4	44.9	45.5	49.0	46.9	45.8
17	23.5	25.5	27.4	28.6	27.9	28.3	28.5	28.9	28.5
16	13.5	13.3	14.4	14.2	13.3	13.1	14.9	14.7	14.6
15	6.2	6.4	5.3	5.9	5.5	5.7	6.3	6.6	7.0
14	3.4	3.6	3.0	4.0	2.6	3.0	4.0	4.0	3.8
12	0.7	0.9	0.7	0.5	0.7	0.5	0.9	0.5	0.5
8	0.2	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1
4	0.1	0.1	0.2	0.0	0.1	0.0	0.1	0.1	0.1

Feed to Rectifying Column - 58.2
Product from Rectifying Column - 189.1
Heads from Rectifying Column - 192.0

TABLE XXXII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	15	30	20	--	20	20	25
42	25	100	90	120	150	220	150	150
38	90	550	350	400	1,000	1,500	1,000	500
34	300	1,200	3,000	4,000	2,500	2,500	2,000	2,000
30	700	5,000	4,500	5,000	5,000	5,500	6,000	4,000
26	2,000	7,500	8,500	9,000	8,000	10,500	8,500	7,500
24	4,000	9,500	9,500	11,500	9,500	11,500	10,500	9,500
23	4,500	10,000	10,000	12,000	11,500	12,500	11,500	9,500
22	4,500	8,500	9,000	12,000	8,500	11,000	10,500	9,000
21	4,000	5,500	6,000	9,000	9,000	7,500	9,500	7,000
20	3,000	3,500	--	6,500	5,200	6,000	5,500	5,000
19	1,000	500	1,100	2,000	3,000	2,500	2,500	2,500
18	300	250	350	400	600	480	500	400
17	200	180	200	300	450	350	400	300
16	50	140	110	125	230	200	200	150
15	50	70	70	80	130	90	80	70
14	30	50	60	45	80	70	60	50
12	45	25	25	25	45	50	25	25
8	5	10	10	0	10	15	15	10
4	0	10	15	0	10	5	5	5

Feed to Rectifying Column - 120
Product from Rectifying Column - 135
Heads from Rectifying Column - 20

TABLE XXXIII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 30% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced							
	0 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.4	191.1	191.1	191.1	191.3	191.1	191.3	191.3
42	188.1	186.9	187.4	186.7	185.6	186.7	187.4	186.7
38	185.0	182.2	183.3	181.3	180.8	181.1	182.7	182.3
34	181.0	175.1	175.1	173.4	173.1	172.9	175.4	173.1
30	174.6	165.3	162.6	162.6	163.5	161.0	164.6	163.6
26	163.7	151.1	145.9	147.8	149.3	146.6	149.4	145.9
24	153.9	140.4	133.2	138.5	138.2	138.0	138.7	138.5
23	144.6	132.2	124.4	132.4	131.2	131.2	132.2	131.0
22	134.8	122.3	112.7	126.0	122.2	124.2	124.4	121.9
21	110.5	84.4	98.6	106.4	103.3	103.1	103.1	102.1
20	91.0	--	86.7	84.8	--	84.2	84.7	85.9
19	56.6	57.5	53.1	55.1	62.4	52.4	56.0	52.3
18	42.1	41.4	41.7	42.6	46.7	46.0	44.5	41.9
17	26.8	25.4	23.7	25.4	32.5	26.5	28.0	26.1
16	14.9	16.3	16.1	14.7	19.6	16.1	17.1	16.0
15	6.8	8.1	8.1	7.7	10.6	8.1	8.7	7.6
14	9.2	5.3	5.7	4.3	5.9	5.5	5.7	5.3
12	2.6	2.0	1.2	1.3	1.5	1.4	1.2	1.0
8	0.2	0.0	0.1	0.0	0.1	0.2	0.1	0.1
4	0.1	0.0	0.1	0.1	0.0	0.2	0.0	0.1

Feed to Rectifying Column - 58.7
Product from Rectifying Column - 186.3
Heads from Rectifying Column - 191.6

TABLE XXXIV

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 30% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	15	65	65	50	50	45	60	50	50
46	35	355	405	245	270	210	330	370	315
42	70	1,050	1,350	900	950	850	1,400	1,300	1,150
40	240	1,600	1,800	1,300	1,500	1,500	1,850	1,950	1,450
38	335	2,050	1,800	1,550	1,700	1,750	2,250	2,100	1,300
36	455	2,750	1,700	1,550	1,800	2,100	2,000	1,750	1,200
34	400	2,900	1,550	1,400	1,550	2,100	1,800	1,450	1,300
32	750	2,700	1,200	1,300	1,100	1,450	1,200	1,050	950
30	1,100	2,750	1,300	950	1,150	1,400	1,350	1,050	1,000
28	1,550	2,700	1,050	1,050	1,050	1,150	1,300	1,100	1,000
26	1,950	2,600	1,200	1,000	1,100	1,250	1,200	900	950
24	1,800	2,300	1,100	900	850	1,000	1,250	850	850
22	1,150	2,450	1,150	990	850	1,000	1,200	900	750
20	795	2,300	900	910	750	1,000	900	700	600
18	135	260	145	110	125	155	140	135	135
16	95	190	89	95	70	105	105	90	70
14	35	50	25	30	20	45	45	35	35
10	0	0	0	0	0	5	5	5	5
6	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 75
Product from Rectifying Column - 370
Heads from Rectifying Column - 40

TABLE XXXV

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 30% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	188.3	185.9	185.4	185.8	186.0	186.1	186.0	185.9	186.0
46	186.0	178.3	178.3	177.3	179.4	178.5	179.9	179.1	177.7
42	175.5	168.3	167.7	167.1	167.0	166.6	165.9	167.0	165.0
40	167.5	158.9	158.9	159.9	158.0	158.3	159.1	159.4	158.6
38	159.6	144.8	145.7	145.1	146.7	144.2	145.7	146.8	143.7
36	139.9	132.2	130.6	131.9	131.1	130.6	131.6	130.9	128.2
34	135.5	126.1	128.5	125.5	124.0	126.1	124.5	124.0	125.2
32	128.7	122.0	121.3	120.1	117.2	119.8	116.0	119.3	118.8
30	120.6	113.4	113.4	111.1	109.3	110.3	109.3	111.0	109.8
28	116.3	111.9	111.3	109.3	106.2	109.1	107.2	109.9	107.7
26	114.1	108.3	107.7	106.6	104.1	105.8	105.2	105.3	104.6
24	111.8	101.1	100.8	103.1	102.2	101.1	101.1	101.9	100.0
22	100.6	98.9	99.4	96.3	94.9	95.3	96.4	95.8	96.3
20	89.7	90.1	92.3	91.0	89.7	90.9	92.8	90.0	91.8
18	57.1	59.0	58.0	58.5	59.5	56.8	57.1	59.1	58.5
16	47.3	46.3	50.4	45.1	47.7	43.8	45.9	49.1	41.0
14	29.6	28.0	29.6	27.7	25.1	27.3	26.8	26.9	25.1
10	2.8	2.9	3.7	2.6	2.7	3.9	4.0	3.9	3.2
6	0.4	0.8	1.0	1.0	0.8	1.0	0.6	0.6	0.8
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 59.6
Product from Rectifying Column - 178.8
Heads from Rectifying Column - 187.0

TABLE XXXVI

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	0	5	5	—	5	10	5	5	0
42	5	10	10	--	15	20	20	15	20
38	20	30	40	50	55	75	45	40	40
34	65	90	165	170	190	170	160	135	150
30	280	380	500	800	1,050	900	450	500	400
26	800	1,300	1,750	2,200	2,800	2,350	2,150	1,950	2,100
24	1,500	2,250	3,400	4,750	5,850	4,900	4,050	3,850	3,850
23	2,300	3,150	4,500	6,850	7,850	6,750	5,500	4,750	5,400
22	2,850	4,300	6,300	8,400	8,500	8,000	8,500	6,300	6,750
21	3,000	4,950	7,150	9,250	9,700	9,300	8,850	7,000	7,300
20	3,850	6,150	7,450	9,600	11,000	9,500	9,150	7,800	8,250
19	1,200	2,400	2,800	6,350	7,000	5,400	3,750	3,100	3,900
18	485	850	950	1,200	2,150	1,350	900	900	800
17	200	370	370	685	890	660	510	510	505
16	55	110	140	165	210	160	140	125	140
15	25	35	40	60	70	70	65	50	55
14	10	15	25	55	60	40	30	30	40
12	0	5	5	30	30	5	5	20	35
8	0	0	0	30	30	0	0	—	0
4	0	0	0	30	35	0	0	—	0

Feed to Rectifying Column - 65
Product from Rectifying Column - 15
Heads from Rectifying Column - 5

TABLE XXXVII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.3	192.4	192.3	191.2	192.1	192.2	192.4	192.4	192.4
42	190.5	190.5	190.3	189.8	190.5	190.2	190.2	190.5	190.2
38	189.2	188.7	188.7	187.3	188.5	188.4	188.8	188.4	188.7
34	183.1	186.7	185.9	185.2	186.0	186.2	185.7	186.4	186.7
30	176.5	183.1	182.1	181.7	181.6	182.3	182.1	182.3	182.5
26	173.9	177.0	175.1	173.6	174.1	174.8	174.7	175.1	175.3
24	170.0	170.7	168.1	166.2	166.1	167.9	167.2	168.3	168.3
23	164.6	164.7	163.1	160.5	160.5	162.3	162.0	163.0	163.9
22	157.4	159.4	157.0	154.1	155.0	156.0	155.0	157.1	156.7
21	142.4	147.0	141.6	143.0	143.6	144.3	144.5	142.8	145.9
20	124.6	131.4	125.5	129.5	131.0	130.6	129.1	125.6	131.4
19	84.5	84.4	79.8	89.8	92.1	82.1	86.0	81.9	85.3
18	48.5	54.2	47.0	47.3	47.0	46.1	45.0	43.6	45.5
17	19.1	23.6	17.5	20.3	19.4	16.9	20.3	22.3	14.9
16	7.5	10.0	8.0	8.1	8.0	6.5	8.2	8.6	6.0
15	2.7	2.5	1.6	2.3	2.3	2.3	2.4	3.3	2.7
14	0.0	0.7	0.0	2.1	1.7	1.3	0.5	1.6	1.6
12	0.0	0.0	0.0	0.7	0.2	0.0	0.0	0.0	0.9
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 77.2
Product from Rectifying Column - 190.3
Heads from Rectifying Column - 190.7

TABLE XXXVIII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	10	5	0	10	10	10	5	--
42	10	15	25	30	25	--	--	35	30
38	40	65	100	125	110	130	135	125	125
34	160	185	325	200	395	260	215	310	160
30	500	580	1,200	1,200	1,150	1,350	1,400	1,300	1,400
26	1,200	2,000	3,100	3,400	3,700	3,750	4,650	4,250	4,450
24	2,350	3,650	4,800	6,100	6,400	6,550	5,850	5,850	6,600
23	3,050	3,950	6,950	7,550	8,250	8,900	8,800	8,200	8,450
22	3,850	5,350	7,100	9,000	9,500	9,350	8,850	8,900	8,800
21	4,150	5,800	8,100	9,100	9,850	10,400	11,500	11,600	10,600
20	3,650	5,500	6,750	8,300	9,800	10,300	--	11,400	10,400
19	1,000	1,950	2,950	2,950	4,850	4,250	5,550	4,700	4,800
18	295	630	600	750	800	1,050	1,250	950	900
17	180	290	405	605	625	760	760	740	550
16	40	70	105	130	120	170	170	175	140
15	20	30	50	75	75	65	70	70	70
14	10	15	50	30	45	25	60	55	45
12	0	15	25	5	40	5	10	35	25
8	15	35	25	20	35	0	30	0	45
4	10	25	30	40	45	0	40	65	45

Feed to Rectifying Column - 60
Product from Rectifying Column - 25
Heads from Rectifying Column - 5

TABLE XXXIX

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.4	192.2	192.1	191.9	191.9	192.1	191.9	192.6	191.6
42	190.0	189.6	189.0	189.0	189.5	188.3	189.5	189.8	189.6
38	187.9	187.0	186.8	186.5	186.8	185.7	186.3	186.7	186.0
34	181.4	184.2	183.2	183.2	183.8	182.3	183.1	183.6	183.0
30	180.9	179.7	178.3	178.0	177.9	177.2	177.6	178.1	178.4
26	173.6	171.1	169.1	168.6	168.5	167.3	167.2	167.5	168.7
24	160.9	160.9	160.4	160.1	164.9	159.8	158.7	159.8	160.3
23	--	155.7	154.4	153.5	154.1	153.1	153.6	153.4	153.9
22	152.7	150.8	147.0	147.0	147.8	147.0	146.9	147.3	146.6
21	135.8	135.1	132.8	133.8	133.8	135.2	134.6	135.5	135.5
20	117.6	118.5	114.8	115.8	119.7	119.5	133.2	123.0	122.5
19	78.4	75.6	74.5	77.2	83.7	82.5	87.5	84.2	83.8
18	42.1	44.6	44.1	44.4	50.8	52.6	44.7	45.3	51.9
17	20.9	20.7	24.5	16.4	29.8	24.1	28.1	32.7	25.7
16	7.1	9.2	9.5	7.1	7.4	9.2	10.7	10.7	8.1
15	3.1	3.7	4.9	3.3	4.2	3.0	3.5	3.1	2.6
14	0.7	0.8	2.1	0.9	0.7	1.0	2.5	1.8	1.8
12	0.0	0.6	0.8	0.0	0.4	0.0	0.1	0.3	0.9
8	0.4	0.4	0.0	0.0	0.2	0.0	0.0	0.0	0.0
4	0.4	0.2	0.0	0.5	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 78.5
Product from Rectifying Column - 189.6
Heads from Rectifying Column - 192.4

TABLE XL

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	10	15	15	15	15	10	10	0	0
42	20	35	65	70	75	65	70	65	70
38	75	200	300	350	400	400	350	300	350
34	300	600	800	950	1,000	500	650	1,000	1,200
30	700	1,000	2,000	2,000	2,000	2,500	2,400	2,500	2,400
26	2,000	3,000	4,000	4,500	5,000	5,500	5,800	5,700	5,500
24	2,500	4,500	5,500	6,000	7,000	7,500	7,600	8,100	7,500
23	2,650	5,200	6,000	6,500	7,500	8,500	8,500	8,700	7,900
22	2,900	5,500	6,500	6,500	7,500	9,000	8,900	8,700	8,100
21	2,850	5,100	6,500	5,500	6,000	7,000	7,500	8,100	6,600
20	2,000	2,500	5,000	5,000	5,500	5,500	6,400	6,900	4,900
19	1,000	1,000	2,000	1,500	1,000	2,250	2,100	2,200	1,550
18	350	550	700	550	800	770	650	730	580
17	150	250	400	300	450	550	500	350	300
16	40	50	100	100	150	200	200	150	200
15	15	40	50	50	65	80	80	65	55
14	5	20	30	30	40	40	35	40	35
12	0	5	5	10	10	10	5	10	5
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 70
Product from Rectifying Column - 65
Heads from Rectifying Column - 20

TABLE XLI

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.2	191.2	191.1	191.2	191.2	191.1	191.1	191.2	191.2
42	187.6	187.5	187.4	187.0	187.0	187.1	187.0	187.1	187.0
38	183.8	183.2	183.0	182.4	182.4	182.4	182.6	182.6	182.4
34	177.3	177.3	177.4	176.9	176.5	176.9	176.7	176.5	176.5
30	172.2	172.0	171.4	169.5	169.1	168.9	169.1	168.7	169.1
26	162.8	162.2	160.3	158.1	157.4	157.4	157.4	157.2	157.0
24	152.5	152.5	151.6	149.8	148.8	148.9	147.7	147.7	147.7
23	144.6	144.6	143.6	143.0	141.5	142.4	141.3	140.5	140.8
22	137.6	137.4	137.7	135.9	134.3	137.1	135.5	134.3	134.0
21	125.1	124.3	125.0	123.2	122.0	117.0	117.0	117.5	117.4
20	112.4	112.8	111.3	110.8	110.6	110.3	109.5	108.8	109.0
19	82.0	82.8	82.7	82.6	82.9	82.7	82.6	83.0	82.8
18	61.6	61.8	62.2	60.0	59.0	63.2	60.5	59.9	61.5
17	35.2	35.6	36.5	36.2	35.5	36.8	36.6	36.0	35.4
16	15.3	15.8	17.8	15.8	17.4	18.8	18.5	17.4	18.3
15	6.1	7.2	6.6	7.2	7.4	8.1	7.5	6.6	6.8
14	2.6	2.6	3.4	3.4	3.8	3.6	3.5	3.3	3.3
12	0.1	0.2	0.5	0.6	0.4	0.4	0.2	0.1	0.4
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 78.4
Product from Rectifying Column - 187.0
Heads from Rectifying Column - 191.2

TABLE XLII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Synthetic Feed Low in Fusel Oil - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	5	5	5	5	10	5	5	15
42	20	35	30	40	50	40	45	40	40
38	75	90	120	155	185	155	165	155	155
34	180	250	350	450	600	450	500	480	500
30	450	500	600	800	1,070	960	880	770	800
26	650	1,000	1,400	1,800	2,300	2,000	1,950	1,800	1,800
24	900	1,800	2,200	1,600	3,300	2,950	3,050	2,750	2,550
23	1,050	2,100	2,400	3,080	3,600	3,500	3,270	3,225	2,650
22	1,100	2,250	2,900	3,400	3,600	3,750	3,450	4,180	3,150
21	1,000	2,050	2,860	3,350	3,090	3,450	3,050	3,050	2,790
20	850	--	2,150	3,250	2,300	3,250	3,250	2,750	2,200
19	380	600	450	550	950	850	600	550	670
18	75	350	450	575	350	420	330	625	325
17	90	225	250	450	200	250	200	250	225
16	30	80	90	175	65	90	65	100	110
15	10	30	40	60	30	40	35	35	45
14	0	10	15	30	15	25	20	25	30
12	0	0	0	5	10	5	0	0	10
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 30
Product from Rectifying Column - 30
Heads from Rectifying Column - 10

TABLE XLIII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Synthetic Feed Low in Fusel Oil - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.2	191.4	191.2	191.3	191.1	191.4	191.3	191.2	191.3
42	187.6	188.3	187.7	187.6	187.5	187.6	187.4	187.6	187.5
38	183.5	184.3	183.9	183.4	182.5	183.6	183.0	182.8	183.2
34	178.8	179.7	179.7	178.6	178.1	179.1	178.6	178.8	178.1
30	172.3	173.4	173.8	172.5	171.2	172.1	171.9	172.3	171.6
26	164.0	166.3	165.3	163.4	162.6	162.6	163.0	162.1	163.2
24	154.8	155.3	155.8	154.9	152.2	152.8	153.2	153.4	153.7
23	149.7	152.5	150.1	151.4	147.0	147.6	147.0	147.6	147.2
22	141.8	145.8	143.5	143.9	140.6	140.8	140.3	140.8	140.2
21	130.3	132.8	131.5	132.4	129.1	128.2	128.0	129.1	128.4
20	114.8	111.4	113.5	112.0	110.7	111.3	110.5	113.6	113.2
19	83.2	84.8	84.1	84.0	83.5	83.0	83.2	84.7	83.9
18	70.7	69.3	70.5	71.7	68.0	66.8	67.6	67.0	67.8
17	47.3	45.7	44.8	49.1	45.5	44.6	46.0	47.8	47.1
16	24.0	22.3	22.0	26.5	25.5	24.6	23.8	25.7	26.5
15	12.4	11.0	10.6	11.7	10.1	9.7	10.3	9.7	12.4
14	4.3	4.5	4.0	5.8	5.0	5.2	5.6	5.6	6.3
12	0.2	0.2	0.2	0.5	0.2	0.5	0.5	0.5	0.5
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 78.5
Product from Rectifying Column - 187.6
Heads from Rectifying Column - 191.3

TABLE XLIV

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed Enriched with Fusel Oil - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	20	15	15	10	10	10	10	10	15
42	15	50	95	80	85	85	80	70	80
38	100	400	600	550	600	500	450	500	500
34	400	800	1,250	1,300	1,550	1,400	1,100	1,200	1,350
30	500	2,000	3,500	3,600	5,550	3,800	3,800	3,500	3,650
26	3,000	5,500	8,500	8,600	9,800	9,000	8,500	7,900	8,100
24	4,500	8,500	10,500	12,300	13,600	13,500	12,100	11,500	11,400
23	5,500	8,500	11,300	13,500	15,500	14,800	13,300	13,000	12,900
22	6,000	8,500	12,000	14,200	16,100	15,000	14,900	14,400	14,500
21	5,500	8,500	11,200	13,800	15,500	—	14,600	14,100	14,300
20	4,500	7,500	9,000	13,100	14,100	13,200	13,500	13,900	13,100
19	1,500	2,000	3,500	5,900	5,400	6,300	5,700	5,400	5,250
18	450	950	1,000	1,600	2,350	2,350	1,800	2,150	1,650
17	250	200	600	800	1,000	1,000	1,000	900	1,100
16	60	120	180	330	370	460	440	400	380
15	25	50	75	50	100	100	100	100	100
14	10	20	40	50	55	90	75	80	70
12	0	5	5	15	15	20	15	15	15
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 140
Product from Rectifying Column - 70
Heads from Rectifying Column - 20

TABLE XLV

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed Enriched with Fusel Oil - 40% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.1	191.3	191.4	191.1	190.7	191.3	191.1	191.3	191.3
42	188.3	187.7	187.7	187.7	187.7	187.9	187.7	188.2	188.0
38	183.8	183.8	183.3	182.7	183.0	183.3	183.6	183.5	183.6
34	178.2	178.8	177.5	177.8	177.4	177.8	178.4	178.4	178.4
30	171.2	171.0	168.9	169.5	169.5	169.5	169.5	170.1	170.0
26	158.2	157.4	156.9	156.3	156.3	156.0	156.3	157.4	157.4
24	148.9	148.1	146.0	147.5	145.0	146.5	146.9	148.1	148.3
23	143.5	142.9	139.7	141.3	139.7	140.4	140.7	141.8	141.8
22	137.7	136.0	135.1	136.0	135.7	136.0	136.3	135.2	135.6
21	121.9	122.5	121.9	125.0	125.1	124.8	125.1	124.9	125.3
20	102.5	106.8	108.5	113.6	115.1	114.9	115.1	115.5	114.9
19	82.9	83.8	84.7	88.7	88.6	89.3	89.5	87.6	88.5
18	56.6	56.9	60.2	60.1	60.8	60.3	60.1	60.5	59.0
17	27.9	27.4	30.0	30.6	30.4	30.0	31.0	28.5	31.0
16	13.7	12.7	15.6	14.0	15.1	15.4	16.0	15.4	16.0
15	4.9	5.8	4.5	5.7	4.1	5.0	5.8	5.8	5.5
14	1.9	1.8	2.5	2.7	2.5	2.5	2.6	2.7	2.5
12	0.3	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.4
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 78.7
Product from Rectifying Column - 187.7
Heads from Rectifying Column - 191.3

TABLE XLVI

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 40% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	45	55	70	---	70	70	70	65	60
46	150	350	350	350	350	350	300	300	250
42	650	1,200	800	500	500	500	400	400	400
40	1,000	1,300	800	500	500	550	450	450	400
38	1,200	1,100	800	550	500	550	500	400	400
36	1,750	950	700	550	500	600	500	450	450
34	1,900	950	650	500	550	550	500	450	450
32	2,000	650	500	500	500	550	450	400	400
30	2,000	650	500	550	500	550	450	400	400
28	2,000	650	500	500	500	550	450	400	400
26	2,000	650	500	500	500	550	400	400	400
24	2,000	550	450	500	500	450	350	325	350
22	2,000	500	450	500	450	400	300	320	350
20	1,800	450	400	450	400	350	250	250	300
18	250	150	150	100	150	150	100	100	100
16	35	40	40	40	35	30	30	30	25
14	10	10	10	5	5	10	5	5	5
10	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 100
Product from Rectifying Column - 350
Heads from Rectifying Column - 55

TABLE XLVII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 40% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	188.5	188.0	188.0	187.9	186.4	186.7	187.0	186.3	186.6
46	183.2	183.0	182.4	181.3	180.0	180.6	180.3	180.0	180.7
42	170.7	170.6	169.1	168.7	168.3	168.5	168.1	168.7	168.3
40	163.7	162.0	161.2	160.3	159.8	159.9	160.4	159.3	160.0
38	156.4	155.1	154.3	153.7	153.1	152.7	153.2	153.6	152.8
36	150.0	149.2	148.0	146.9	146.0	146.3	147.0	146.0	146.4
34	142.6	142.1	141.1	139.0	139.1	138.9	139.3	139.7	139.0
32	134.4	134.1	133.6	132.1	132.4	131.9	131.9	139.2	139.9
30	128.2	128.0	127.5	126.9	126.3	126.0	126.6	126.9	126.4
28	124.6	124.0	123.6	122.8	123.0	122.8	122.4	122.8	122.5
26	120.3	120.0	119.3	118.3	118.0	118.6	118.1	118.8	118.0
24	109.5	109.0	108.5	107.9	107.6	108.0	108.2	107.7	107.8
22	100.0	99.6	99.7	98.6	98.2	98.9	98.4	98.3	98.8
20	88.6	88.0	87.5	86.3	86.0	86.6	86.4	86.0	86.4
18	67.2	66.8	66.1	65.0	65.7	65.3	65.9	65.1	65.5
16	38.2	37.7	37.0	36.8	36.1	36.8	37.0	36.3	36.7
14	18.2	17.3	17.0	16.6	16.6	17.1	16.3	16.8	16.8
10	7.3	7.0	7.0	6.4	6.8	6.2	6.5	6.7	6.0
6	1.7	1.4	1.1	1.0	0.9	1.0	0.8	1.2	1.1
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6

Feed to Rectifying Column - 79.0
Product from Rectifying Column - 180.0
Heads from Rectifying Column - 186.8

TABLE XLVIII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	10	10	10	10	10	10	10	10	10
42	10	15	15	15	15	15	10	10	10
38	25	35	40	45	40	35	30	30	30
34	85	150	165	180	180	165	150	120	115
30	275	525	580	710	690	600	520	450	410
26	750	1,600	2,100	2,200	2,350	1,950	1,800	1,400	1,400
24	1,650	3,100	3,450	3,900	3,900	3,550	3,100	2,700	2,600
23	2,500	3,900	4,400	5,000	5,200	4,900	4,150	3,450	3,450
22	3,150	4,800	5,500	5,700	6,700	5,650	4,750	4,300	4,200
21	3,850	6,000	7,250	7,700	8,900	6,900	5,900	5,450	5,300
20	4,300	6,100	7,900	8,800	9,770	7,400	7,150	6,100	5,900
19	3,900	5,600	7,200	8,600	9,240	7,100	6,500	5,850	5,350
18	1,250	1,600	2,200	3,900	4,300	2,850	2,650	2,100	2,050
17	280	450	600	1,500	1,650	1,000	900	600	550
16	100	185	245	295	410	240	250	145	160
15	20	45	55	70	100	70	60	40	35
14	10	15	25	35	30	20	25	10	20
12	0	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 70
Product from Rectifying Column - 15
Heads from Rectifying Column - 15

TABLE XLIX

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.0	192.1	192.2	192.0	192.0	192.1	192.1	192.1	192.1
42	190.1	190.0	190.1	190.0	190.1	190.1	190.1	190.0	190.2
38	188.3	188.3	188.4	188.3	188.3	188.5	188.3	188.5	188.5
34	185.7	185.8	185.8	185.9	185.9	186.0	186.0	186.0	186.0
30	182.3	182.0	182.1	182.0	182.0	182.2	182.3	182.3	182.4
26	176.7	176.6	176.9	176.7	176.5	176.9	176.9	176.9	176.9
24	170.0	169.1	170.0	169.4	169.2	170.0	169.8	170.0	169.9
23	166.3	165.7	166.2	166.2	165.7	165.7	166.2	167.3	167.3
22	160.5	161.0	161.0	161.1	160.4	160.6	160.8	161.4	161.4
21	149.6	149.8	149.6	149.7	150.2	150.4	150.8	150.8	151.5
20	139.6	140.2	142.3	142.3	140.4	140.4	142.5	142.3	139.9
19	108.2	109.2	114.5	116.7	118.2	117.5	117.5	117.2	115.5
18	68.1	69.6	76.7	77.4	75.6	71.6	70.4	70.7	73.2
17	23.1	22.6	26.8	41.1	38.7	35.9	37.0	33.2	31.7
16	15.3	8.5	10.4	12.6	13.5	12.1	13.1	10.8	10.4
15	4.3	3.1	2.2	3.9	3.4	3.6	3.4	2.6	2.4
14	1.4	1.2	0.9	1.4	1.1	0.8	1.4	1.3	1.0
12	0.1	0.1	0.1	0.0	0.2	0.0	0.0	0.1	0.1
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 98.3
Product from Rectifying Column - 189.8
Heads from Rectifying Column - 191.6

TABLE L

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 50% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	10	10	15	15	15	15	20	15
42	5	15	20	30	25	25	20	25	25
38	15	30	65	65	75	75	70	75	70
34	60	230	250	300	360	320	310	330	320
30	150	360	720	800	1,050	1,000	980	900	890
26	430	1,250	2,150	2,450	3,000	2,800	2,600	2,250	2,500
24	700	2,100	3,650	3,800	4,250	4,200	3,500	3,650	3,800
23	1,000	2,900	4,400	5,100	5,600	5,100	4,400	4,850	4,750
22	1,100	3,500	5,050	6,300	6,900	5,950	5,800	5,750	5,900
21	1,200	3,800	6,400	7,650	8,900	7,350	6,800	6,750	6,350
20	1,100	4,200	6,900	8,300	9,040	8,000	7,350	6,850	6,600
19	500	3,650	6,900	8,000	8,470	6,900	6,150	6,100	5,400
18	225	1,000	2,850	3,300	4,100	2,500	1,950	2,200	1,850
17	85	440	1,050	1,650	2,300	1,250	950	1,000	750
16	25	50	340	430	580	350	230	260	140
15	5	35	100	140	140	95	65	70	40
14	10	10	25	35	50	30	25	25	10
12	0	0	0	5	5	5	5	0	0
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 70
Product from Rectifying Column - 25
Heads from Rectifying Column - 25

TABLE LI

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 4:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	191.6	191.8	191.7	191.9	191.6	191.6	191.7	191.8	191.6
42	188.4	189.0	188.4	188.9	188.4	188.6	188.6	188.4	188.6
38	186.9	187.0	187.0	187.0	186.9	187.0	186.9	187.0	186.8
34	183.0	183.4	183.4	183.4	183.5	183.3	183.7	183.4	183.4
30	180.0	179.9	180.2	179.9	180.3	179.9	179.8	179.9	180.0
26	173.6	172.7	173.0	172.7	173.0	172.9	172.6	172.9	172.9
24	166.9	166.2	166.3	166.5	166.2	166.5	165.7	166.0	166.4
23	162.2	162.0	161.7	161.9	162.1	161.9	161.4	161.4	161.7
22	156.3	156.0	156.1	156.9	156.0	155.6	155.1	155.9	156.2
21	145.5	146.3	146.1	145.9	145.4	145.9	146.2	145.8	145.6
20	136.8	136.6	135.2	137.4	136.8	137.8	136.0	136.8	136.3
19	105.8	108.7	108.7	110.3	111.1	110.9	111.2	108.1	108.9
18	84.9	87.8	87.8	85.9	84.9	88.0	85.2	84.2	86.6
17	42.0	45.3	46.0	49.2	51.5	46.2	40.9	46.8	43.2
16	14.6	16.9	14.8	18.9	15.5	16.7	14.8	14.1	17.0
15	7.6	6.9	7.4	6.7	8.8	7.4	5.6	4.8	6.8
14	1.7	1.1	0.9	1.0	1.9	2.0	0.9	0.8	0.9
12	0.5	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.3
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 99.8
Product from Rectifying Column - 188.4
Heads from Rectifying Column - 191.6

TABLE LII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed 50% Alcohol at Plate 18; Reflux Ratio 3:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced						
	0 hrs.	3 hrs.	6 hrs.	12 hrs.	15 hrs.	21 hrs.	24 hrs.
50	5	5	10	10	10	5	5
42	15	20	35	55	65	65	60
38	45	95	180	275	305	340	305
34	125	295	505	700	900	880	875
30	380	765	1,300	1,900	2,000	2,050	1,950
26	930	1,700	2,650	4,000	4,200	3,700	4,950
24	1,250	2,500	3,950	5,600	6,900	7,600	7,400
23	1,750	2,950	5,050	7,350	8,250	8,950	8,700
22	1,750	3,550	5,900	7,700	8,400	9,350	9,700
21	1,850	3,850	6,100	8,700	9,400	10,000	9,900
20	1,550	3,450	5,900	8,300	8,550	9,900	10,000
19	900	2,250	3,700	6,700	7,650	8,450	7,350
18	405	715	900	3,000	2,500	2,400	2,450
17	125	375	570	1,950	1,500	1,400	900
16	30	85	110	840	535	550	320
15	10	25	50	185	115	120	90
14	0	10	20	75	45	40	40
12	0	0	0	5	0	5	5
8	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0

Feed to Rectifying Column - 110
Product from Rectifying Column - 60
Heads from Rectifying Column - 70

TABLE LIII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 3:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced						
	0 hrs.	3 hrs.	6 hrs.	12 hrs.	15 hrs.	21 hrs.	24 hrs.
50	191.3	191.4	191.6	191.3	191.4	191.3	191.5
42	188.2	187.8	188.0	187.7	187.8	187.8	187.8
38	184.7	184.5	184.6	184.1	184.3	184.5	184.1
34	181.0	180.0	181.4	180.9	180.3	181.0	180.6
30	176.2	176.2	176.7	176.9	177.7	177.1	176.4
26	167.0	166.0	166.7	166.6	167.2	166.7	167.2
24	160.8	159.8	160.1	159.6	159.6	160.1	159.6
23	155.0	154.7	154.8	155.8	154.2	154.4	154.7
22	149.0	148.4	147.1	148.1	148.0	149.3	148.1
21	134.6	135.0	135.1	137.3	136.6	136.0	136.1
20	122.3	123.0	122.3	115.1	114.4	113.7	114.2
19	109.6	109.7	112.2	115.1	114.4	113.7	114.2
18	75.6	76.1	76.9	73.9	75.3	78.1	76.3
17	42.4	40.7	43.3	38.7	43.1	40.2	38.4
16	22.4	20.1	24.2	18.9	21.1	19.7	22.0
15	6.2	6.5	6.9	8.3	6.9	7.0	5.1
14	1.3	3.2	2.4	4.0	4.6	3.8	2.2
12	0.2	0.3	0.2	0.3	0.3	0.5	0.3
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 99.1
Product from Rectifying Column - 187.8
Heads from Rectifying Column - 191.6

TABLE LIV

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced							
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	55	55	55	55	50	50	55	55
46	280	260	260	240	250	240	240	240
42	350	300	320	310	280	310	340	310
40	370	320	320	320	300	285	320	310
38	380	390	340	350	330	315	330	300
36	440	400	380	400	380	370	390	330
34	440	410	360	380	370	250	400	350
32	270	290	245	340	265	250	360	280
30	230	240	195	320	220	230	380	225
28	190	190	160	285	170	180	330	170
26	140	160	150	220	140	125	290	120
24	140	120	120	180	100	95	230	85
22	150	100	105	140	90	80	175	75
20	120	90	100	120	75	95	140	85
18	100	120	110	140	120	120	130	140
16	30	40	28	35	22	36	31	35
14	0	5	0	0	0	5	0	0
10	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 140
Product from Rectifying Column - 260
Heads from Rectifying Column - 58

TABLE LV

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 50% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced							
	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	187.9	186.9	187.2	187.8	187.0	187.1	187.2	187.2
46	181.7	180.0	181.2	181.8	180.7	180.9	181.2	181.4
42	173.2	170.9	172.9	172.5	173.0	173.3	172.8	173.1
40	166.5	165.0	166.0	165.7	166.2	166.7	165.9	166.2
38	161.0	158.7	159.7	159.0	161.6	160.0	157.9	160.8
36	156.5	154.2	156.7	155.1	157.0	153.8	153.7	156.3
34	151.3	149.2	150.1	148.7	151.0	148.0	149.4	151.9
32	146.6	144.2	146.1	143.5	145.0	143.6	144.9	146.3
30	142.7	141.0	143.0	140.0	142.5	140.1	141.8	143.0
28	139.2	137.7	139.0	137.1	139.5	136.9	139.0	139.9
26	135.6	133.9	135.6	134.0	135.5	133.7	135.1	135.4
24	129.6	126.0	129.1	128.3	129.3	127.0	129.9	130.3
22	122.9	119.2	123.1	122.0	122.6	120.6	124.0	124.1
20	112.0	108.7	113.7	111.9	112.7	110.3	112.9	113.3
18	86.9	84.2	89.0	88.8	89.2	85.3	86.7	87.2
16	46.0	43.3	48.3	47.7	48.0	45.1	46.2	46.6
14	26.8	23.8	27.9	27.0	28.2	24.4	26.6	26.4
10	9.5	7.1	9.9	10.0	10.3	8.3	9.0	9.1
6	2.1	2.0	2.3	2.0	2.6	1.8	2.4	2.6
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 99.5
Product from Rectifying Column - 181.2
Heads from Rectifying Column - 187.2

TABLE LVI

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 60% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	5	5	5	5	5	5	5	5	5
42	10	10	15	15	15	--	--	15	15
38	15	30	40	50	60	60	55	45	50
34	40	95	160	175	225	200	195	180	200
30	95	345	520	590	740	670	670	630	645
26	320	900	1,500	1,600	2,350	2,100	1,900	1,600	1,700
24	400	2,050	2,850	3,300	3,950	3,700	3,700	3,300	3,000
23	800	2,600	3,550	4,300	5,250	4,900	4,750	4,500	3,900
22	1,100	3,250	4,300	5,250	6,400	6,050	5,750	5,450	4,900
21	1,400	4,000	5,500	6,800	8,200	7,600	7,250	7,000	6,450
20	1,800	4,750	6,250	8,000	9,750	9,200	8,150	8,250	7,050
19	1,850	4,950	6,450	9,300	10,650	9,450	8,850	8,700	7,900
18	550	2,550	3,500	5,900	6,700	7,050	6,350	5,950	3,800
17	280	550	1,700	4,150	4,850	5,050	4,450	2,850	1,800
16	30	170	275	1,000	1,590	1,745	1,390	670	370
15	5	45	80	165	295	380	295	180	95
14	--	10	20	60	90	145	115	55	35
12	0	0	0	0	5	5	5	0	0
8	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 95
Product from Rectifying Column - 15
Heads from Rectifying Column - 5

TABLE LVII

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 60% Alcohol at Plate 18; Reflux Ratio - 5:1; Product - Plate 42

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	192.2	192.2	192.3	192.4	192.2	192.2	192.2	192.3	192.4
42	189.9	189.9	190.0	190.1	189.9	190.0	190.0	190.0	190.0
38	188.2	188.2	188.2	188.2	188.1	188.2	188.1	188.3	188.2
34	185.5	185.6	185.7	185.7	185.3	185.6	185.5	185.7	185.7
30	183.0	182.6	182.1	182.4	182.1	182.1	182.1	182.4	182.6
26	177.7	177.6	176.7	177.2	176.5	176.4	176.4	177.0	177.0
24	172.0	171.5	171.4	171.7	171.0	170.8	171.0	171.1	171.7
23	168.2	167.6	167.2	167.8	167.0	167.2	167.2	167.7	167.9
22	164.9	163.6	163.8	164.5	163.4	163.6	163.4	163.6	163.9
21	157.8	156.3	156.4	157.7	156.1	157.0	157.0	156.6	156.5
20	147.0	147.7	149.1	150.1	149.5	150.6	150.7	149.9	149.1
19	126.7	124.8	132.8	135.5	134.7	135.9	134.9	134.0	131.5
18	97.2	96.5	104.8	104.9	103.0	105.9	107.0	104.9	102.3
17	70.9	73.4	74.7	79.4	80.2	75.8	76.7	76.6	79.3
16	37.6	36.4	35.1	30.7	32.0	33.2	30.7	34.5	34.0
15	15.0	13.3	14.2	9.0	10.9	10.9	8.4	10.9	11.8
14	3.1	2.7	3.1	2.1	2.5	3.3	2.0	3.2	3.5
12	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.3	0.2
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 119.3
Product from Rectifying Column - 190.0
Heads from Rectifying Column - 192.8

TABLE LVIII

FUSEL OIL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 60% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Fusel Oil Content of Liquid Phase by Plates, mgs. of Amyl Alcohol per 100 ml. of Sample

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	15	25	40	35	20	30	35	40	30
46	25	130	140	230	250	180	155	200	165
42	55	440	625	865	830	570	605	835	710
40	145	625	700	990	700	700	840	1,080	930
38	200	710	840	1,240	1,080	890	1,240	1,190	1,400
36	270	1,000	1,240	1,400	1,510	1,290	1,860	2,190	2,190
34	365	1,450	1,680	2,050	1,510	1,920	2,390	3,090	2,700
32	490	1,400	2,250	2,930	2,760	2,760	3,360	3,860	3,760
30	645	1,800	2,840	3,550	3,000	3,650	3,760	5,200	3,860
28	865	2,690	3,000	3,360	4,290	4,650	5,190	5,850	5,690
26	930	2,590	3,550	4,290	4,910	5,850	6,670	6,670	6,460
24	1,400	2,690	4,180	4,910	6,050	7,650	7,110	7,370	7,990
22	1,920	2,760	3,550	4,290	6,670	7,110	8,640	7,370	8,310
20	2,050	2,700	4,180	3,960	5,350	7,650	9,150	7,370	8,310
18	840	1,240	1,740	2,050	2,630	3,650	3,360	2,690	3,450
16	690	990	2,000	1,860	3,760	5,510	6,260	4,540	5,510
14	60	309	365	490	830	690	962	740	890
10	0	5	5	0	0	10	15	10	15
6	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0

Feed to Rectifying Column - 85
Product from Rectifying Column - 200
Heads from Rectifying Column - 30

TABLE LIX

ALCOHOL DISTRIBUTION IN RECTIFYING COLUMN

Experimental Conditions: Feed - 60% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Apparent Alcohol Content of Liquid Phase by Plates, Degrees Proof at 60°F

Plate	Time of Sampling After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	186.1	188.0	187.8	187.6	188.0	188.1	188.2	187.8	188.0
46	184.8	184.6	184.4	184.6	184.6	184.6	184.3	183.5	183.1
42	179.1	178.4	177.7	176.6	177.9	177.9	177.7	177.7	177.5
40	177.1	175.7	174.6	174.4	175.3	174.8	174.6	174.4	174.7
38	173.3	171.1	169.5	172.0	171.3	170.9	169.9	169.9	170.6
36	168.8	168.2	167.9	166.9	167.9	168.2	168.1	166.8	166.4
34	166.4	165.8	164.4	166.0	165.6	165.0	166.0	164.5	163.9
32	163.2	162.6	161.0	160.1	161.0	160.9	161.3	159.5	160.0
30	158.2	157.5	157.4	156.3	158.0	157.9	157.6	155.3	156.0
28	155.8	154.8	154.3	154.5	155.0	155.0	154.3	154.5	154.2
26	153.0	152.5	152.5	150.9	152.2	151.3	151.4	150.4	150.7
24	148.5	147.0	147.2	146.2	147.6	147.6	147.0	145.4	146.8
22	144.4	142.3	142.4	142.0	142.6	143.2	142.8	141.8	142.3
20	138.6	135.7	135.2	135.2	135.7	136.8	136.6	136.0	136.7
18	109.7	111.1	110.7	110.1	108.9	109.4	109.7	109.4	109.9
16	94.8	94.0	91.1	88.1	95.3	98.0	98.4	95.6	97.1
14	24.0	30.2	25.7	26.2	28.1	30.3	26.8	27.5	29.8
10	0.2	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3
6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Feed to Rectifying Column - 119.5
Product from Rectifying Column - 184.5
Heads from Rectifying Column - 189.2

TABLE LX

TEMPERATURE OF VAPOR PHASE BY PLATES OF RECTIFYING COLUMN

Experimental Conditions: Feed - 60% Alcohol at Plate 18; Reflux Ratio - 2:1; Product - Plate 46

Temperature in Degrees Farenheit

Plate	Time of Reading After Withdrawal of Product Commenced								
	0 hrs.	3 hrs.	6 hrs.	9 hrs.	12 hrs.	15 hrs.	18 hrs.	21 hrs.	24 hrs.
50	172.0	172.0	172.0	172.0	172.0	172.0	172.0	172.0	172.0
48	173.0	173.0	173.0	173.0	173.0	173.0	173.0	173.0	173.0
46	174.0	174.0	174.0	174.0	174.0	174.0	174.0	174.0	174.0
44	174.5	174.5	174.5	174.5	174.5	174.5	174.5	174.5	174.5
42	174.0	174.5	174.5	174.5	174.5	174.5	174.5	174.5	174.5
40	174.0	174.5	174.5	174.5	174.5	174.5	174.5	174.5	174.5
38	174.0	174.5	175.0	175.0	175.0	175.0	175.0	175.0	175.0
36	174.5	175.5	175.5	175.5	176.0	176.0	176.0	176.0	176.0
34	174.5	175.0	176.0	176.0	176.0	176.0	176.0	176.0	176.0
32	175.5	175.5	176.0	176.0	176.5	176.5	176.5	176.5	176.5
30	176.5	176.5	177.0	177.5	177.0	177.5	177.5	177.5	177.5
28	176.5	176.5	177.0	177.5	177.5	177.5	177.5	177.5	177.5
26	179.0	179.5	179.5	180.0	180.0	180.0	180.0	180.0	180.0
24	179.0	179.5	179.5	180.0	180.0	180.0	180.0	180.5	180.5
23	179.0	179.5	179.5	180.0	180.0	180.0	180.0	180.5	180.5
22	179.5	179.5	180.5	180.5	180.0	180.0	180.5	180.5	180.5
21	179.5	179.5	180.5	180.5	180.5	180.5	180.5	180.5	180.5
20	180.5	180.5	181.5	181.5	181.5	181.5	181.5	181.5	181.5
19	182.0	182.0	182.0	182.0	182.0	182.0	182.0	182.5	182.5
16	188.5	189.0	189.0	189.0	189.0	189.0	189.0	189.5	189.5
14	205.0	206.0	206.0	206.0	206.0	206.0	206.0	206.0	206.0
12	214.0	214.0	214.0	214.0	214.0	214.0	214.0	213.5	213.5
6	217.0	217.0	217.0	217.0	217.0	217.0	217.0	217.5	217.5

TABLE LXI

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
0.00	0.000	0.00	0.00	100.00	212.0	0.0	0.000	0.00	0.00
0.50	0.002	0.63	0.64	99.65	211.4	5.3	0.021	6.61	6.64
1.00	0.004	1.26	1.26	98.95	210.1	10.3	0.043	12.76	12.81
1.50	0.006	1.88	1.89	98.55	209.4	14.4	0.062	17.74	17.80
2.00	0.008	2.51	2.52	98.05	208.5	19.2	0.085	23.52	23.59
2.50	0.010	3.14	3.15	97.50	207.5	22.9	0.104	27.91	27.99
3.00	0.012	3.76	3.78	97.11	206.8	26.3	0.122	31.91	31.98
3.50	0.014	4.38	4.40	96.56	205.8	29.9	0.143	36.07	36.14
4.00	0.016	5.00	5.02	96.00	204.8	32.5	0.159	39.03	39.09
4.50	0.018	5.62	5.65	95.63	204.1	35.4	0.177	42.28	42.35
5.00	0.020	6.24	6.26	95.22	203.4	37.5	0.190	44.60	44.67
5.50	0.022	6.86	6.89	94.84	202.7	40.0	0.207	47.33	47.39
6.00	0.024	7.48	7.51	94.56	202.2	41.9	0.220	49.37	49.42
6.50	0.026	8.10	8.13	94.10	201.4	43.7	0.233	51.29	51.35
7.00	0.029	8.71	8.75	93.73	200.7	45.3	0.245	52.97	53.04
7.50	0.031	9.33	9.36	93.40	200.1	46.7	0.255	54.43	54.49
8.00	0.033	9.94	9.98	93.10	199.6	48.1	0.266	55.88	55.94
8.50	0.035	10.56	10.60	92.78	199.0	49.3	0.275	57.12	57.17
9.00	0.037	11.17	11.21	92.42	198.4	50.5	0.285	58.34	58.39
9.50	0.039	11.78	11.82	92.10	197.8	51.6	0.294	59.45	59.50
10.00	0.042	12.39	12.44	91.80	197.2	52.7	0.304	60.55	60.61
10.50	0.044	13.00	13.05	91.46	196.6	53.6	0.311	61.45	61.50
11.00	0.046	13.61	13.66	91.12	196.0	54.6	0.320	62.44	62.50
11.50	0.048	14.22	14.28	90.84	195.5	55.6	0.329	63.43	63.48

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
12.00	0.051	14.83	14.89	90.54	195.0	56.5	0.337	64.31	64.36
12.50	0.053	15.44	15.50	90.30	194.5	57.3	0.344	65.09	65.14
13.00	0.055	16.05	16.10	90.02	194.0	58.1	0.352	65.86	65.91
13.50	0.058	16.65	16.71	89.79	193.6	58.8	0.358	66.54	66.59
14.00	0.060	17.26	17.32	89.56	193.2	59.5	0.364	67.21	67.26
14.50	0.062	17.86	17.92	89.36	192.8	60.1	0.371	67.78	67.83
15.00	0.065	18.47	18.54	89.16	192.5	60.7	0.377	68.36	68.40
15.50	0.067	19.07	19.14	88.94	192.1	61.3	0.383	68.92	68.97
16.00	0.069	19.68	19.74	88.72	191.7	61.9	0.389	69.49	69.53
16.50	0.072	20.28	20.35	88.52	191.3	62.4	0.394	69.96	70.01
17.00	0.074	20.88	20.95	88.32	191.0	62.9	0.399	70.43	70.48
17.50	0.077	21.48	21.55	88.11	190.6	63.4	0.404	70.90	70.94
18.00	0.079	22.08	22.15	87.92	190.3	63.9	0.409	71.36	71.41
18.50	0.082	22.68	22.75	87.77	190.0	64.3	0.413	71.73	71.78
19.00	0.084	23.28	23.35	87.62	189.7	64.8	0.419	72.20	72.23
19.50	0.087	23.88	23.95	87.47	189.4	65.2	0.423	72.56	72.61
20.00	0.089	24.47	24.55	87.32	189.2	65.6	0.427	72.93	72.97
20.50	0.091	25.07	25.14	87.02	188.6	66.0	0.432	73.30	73.34
21.00	0.094	25.66	25.74	86.71	188.1	66.4	0.436	73.66	73.71
21.50	0.096	26.26	26.32	86.41	187.5	66.8	0.440	74.03	74.07
22.00	0.099	26.85	26.92	86.11	187.0	67.2	0.445	74.39	74.44
22.50	0.102	27.44	27.51	86.02	186.8	67.5	0.448	74.66	74.71
23.00	0.105	28.03	28.10	85.94	186.7	67.8	0.452	74.94	74.97.
23.50	0.107	28.62	28.69	85.85	186.5	68.1	0.455	75.21	75.24

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
24.00	0.110	29.21	29.29	85.76	186.4	68.4	0.458	75.48	75.52
24.50	0.113	29.80	29.88	85.67	186.2	68.7	0.462	75.75	75.78
25.00	0.115	30.39	30.46	85.58	186.0	68.9	0.464	75.93	75.96
25.50	0.118	30.97	31.05	85.50	185.9	69.2	0.467	76.20	76.23
26.00	0.121	31.56	31.62	85.41	185.7	69.4	0.470	76.37	76.41
26.50	0.124	32.14	32.21	85.32	185.6	69.7	0.474	76.64	76.68
27.00	0.126	32.72	32.79	85.22	185.4	70.0	0.477	76.91	76.94
27.50	0.129	33.30	33.38	85.13	185.2	70.2	0.480	77.09	77.12
28.00	0.132	33.88	33.95	85.04	185.1	70.4	0.482	77.26	77.30
28.50	0.135	34.46	34.52	84.95	184.9	70.7	0.486	77.53	77.56
29.00	0.138	35.03	35.10	84.86	184.7	70.9	0.488	77.71	77.74
29.50	0.141	35.61	35.68	84.79	184.6	71.1	0.490	77.88	77.92
30.00	0.144	36.18	36.26	84.70	184.5	71.3	0.493	78.06	78.09
30.50	0.147	36.75	36.82	84.62	184.3	71.5	0.495	78.23	78.26
31.00	0.149	37.32	37.39	84.54	184.2	71.7	0.498	78.41	78.44
31.50	0.152	37.89	37.96	84.46	184.0	71.9	0.400	78.58	78.62
32.00	0.155	38.46	38.54	84.37	183.9	72.0	0.502	78.67	78.71
32.50	0.159	39.02	39.09	84.28	183.7	72.2	0.504	78.85	78.88
33.00	0.162	39.59	39.66	84.20	183.6	72.4	0.506	79.02	79.05
33.50	0.165	40.15	40.22	84.12	183.4	72.6	0.509	79.20	79.28
34.00	0.168	40.72	40.78	84.04	183.3	72.8	0.512	79.37	79.40
34.50	0.171	41.28	41.35	83.96	183.1	72.9	0.513	79.46	79.49
35.00	0.174	41.83	41.90	83.87	183.0	73.1	0.515	79.63	79.66
35.50	0.177	42.39	42.46	83.79	182.8	73.2	0.517	79.72	79.75

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL–WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
36.00	0.180	42.94	43.01	83.72	182.7	73.4	0.519	79.89	79.92
36.50	0.184	43.50	43.57	83.65	182.6	73.6	0.522	80.06	80.10
37.00	0.187	44.05	44.11	83.58	182.4	73.7	0.523	80.15	80.18
37.50	0.190	44.60	44.67	83.51	182.3	73.8	0.524	80.24	80.27
38.00	0.193	45.15	45.21	83.44	182.2	74.0	0.527	80.41	80.44
38.50	0.197	45.70	45.76	83.37	182.1	74.2	0.529	80.58	80.62
39.00	0.200	46.24	46.30	83.30	181.9	74.3	0.531	80.67	80.70
39.50	0.203	46.79	46.85	83.24	181.8	74.5	0.533	80.84	80.87
40.00	0.207	47.33	47.39	83.18	181.7	74.6	0.535	80.93	80.96
40.50	0.210	47.87	47.94	83.13	181.6	74.7	0.536	81.01	81.04
41.00	0.214	48.41	48.47	83.07	181.5	74.8	0.537	81.10	81.12
41.50	0.217	48.94	49.01	83.01	181.4	75.0	0.540	81.27	81.30
42.00	0.221	49.48	49.54	82.95	181.3	75.1	0.541	81.36	81.38
42.50	0.224	50.01	50.80	82.89	181.2	75.2	0.543	81.44	81.47
43.00	0.228	50.54	50.61	82.83	181.1	75.4	0.545	81.61	81.64
43.50	0.231	51.08	51.14	82.78	181.0	75.5	0.547	81.70	81.78
44.00	0.235	51.60	51.67	82.72	180.9	75.6	0.548	81.78	81.81
44.50	0.239	52.13	52.19	82.66	180.8	75.7	0.549	81.87	81.89
45.00	0.242	52.66	52.72	82.60	180.7	75.9	0.552	82.04	82.07
45.50	0.246	53.18	53.24	82.54	180.6	76.0	0.553	82.12	82.15
46.00	0.250	53.70	53.77	82.48	180.5	76.1	0.555	82.21	82.23
46.50	0.254	54.23	54.29	82.42	180.4	76.2	0.556	82.29	82.32
47.00	0.258	54.75	54.81	82.37	180.3	76.4	0.559	82.46	82.49
47.50	0.261	55.26	55.32	82.30	180.1	76.5	0.560	82.54	82.58

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL–WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
48.00	0.265	55.78	55.84	82.25	180.0	76.6	0.562	82.63	82.66
48.50	0.269	56.29	56.35	82.19	179.9	76.8	0.564	82.80	82.82
49.00	0.273	56.81	56.87	82.13	179.8	76.9	0.566	82.88	82.91
49.50	0.277	57.32	57.38	82.07	179.7	77.0	0.567	82.97	82.99
50.00	0.281	57.83	57.89	82.02	179.6	77.1	0.568	83.05	83.08
50.50	0.285	58.34	58.39	81.96	179.5	77.2	0.570	83.14	83.16
51.00	0.289	58.84	58.90	81.91	179.4	77.3	0.571	83.22	83.25
51.50	0.293	59.35	59.40	81.86	179.3	77.4	0.573	83.30	83.33
52.00	0.297	59.85	59.91	81.81	179.3	77.5	0.574	83.39	83.42
52.50	0.301	60.35	60.41	81.76	179.2	77.7	0.577	83.56	83.58
53.00	0.305	60.85	60.91	81.70	179.1	77.8	0.578	83.64	83.67
53.50	0.310	61.35	61.41	81.65	179.0	77.9	0.580	83.72	83.75
54.00	0.315	61.85	61.90	81.60	178.9	78.0	0.581	83.80	83.83
54.50	0.319	62.34	62.40	81.55	178.8	78.1	0.583	83.89	83.92
55.00	0.323	62.84	62.89	81.49	178.7	78.2	0.584	83.97	84.00
55.50	0.328	63.33	63.38	81.44	178.6	78.3	0.586	84.06	84.08
56.00	0.332	63.82	63.87	81.38	178.5	78.4	0.587	84.14	84.17
56.50	0.337	64.31	64.36	81.33	178.4	78.6	0.590	84.30	84.33
57.00	0.341	64.80	64.85	81.28	178.3	78.7	0.591	84.39	84.42
57.50	0.346	65.28	65.33	81.23	178.2	78.8	0.593	84.47	84.50
58.00	0.351	65.77	65.82	81.18	178.1	78.9	0.594	84.55	84.58
58.50	0.355	66.25	66.30	81.13	178.0	79.1	0.597	84.72	84.74
59.00	0.360	66.73	66.78	81.08	177.9	79.2	0.599	84.80	84.82
59.50	0.365	67.21	67.26	81.04	177.9	79.3	0.600	84.88	84.91

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
60.00	0.370	67.69	67.73	81.00	177.8	79.4	0.601	84.97	84.99
60.50	0.375	68.17	68.21	80.96	177.7	79.6	0.604	85.13	85.16
61.00	0.380	68.64	68.69	80.91	177.6	79.7	0.606	85.21	85.24
61.50	0.385	69.11	69.16	80.86	177.5	79.8	0.607	85.30	85.32
62.00	0.390	69.59	69.63	80.80	177.4	79.9	0.609	85.38	85.40
62.50	0.395	70.06	70.10	80.74	177.3	80.1	0.612	85.54	85.57
63.00	0.400	70.52	70.57	80.642	177.16	80.3	0.614	85.70	85.72
63.50	0.405	70.99	71.03	80.592	177.06	80.4	0.616	85.79	85.81
64.00	0.410	71.45	71.50	80.541	176.97	80.5	0.618	85.87	85.89
64.50	0.415	71.92	71.96	80.491	176.88	80.6	0.619	85.95	85.98
65.00	0.421	72.38	72.42	80.438	176.79	80.8	0.622	86.11	86.13
65.50	0.426	72.84	72.88	80.391	176.70	80.9	0.624	86.19	86.22
66.00	0.432	73.30	73.33	80.341	176.61	81.1	0.626	86.36	86.38
66.50	0.437	73.76	73.80	80.291	176.52	81.2	0.628	86.44	86.46
67.00	0.443	74.21	74.25	80.237	176.43	81.4	0.631	86.60	86.62
67.50	0.448	74.66	74.71	80.191	176.34	81.5	0.633	86.68	86.70
68.00	0.454	75.11	75.15	80.142	176.26	81.7	0.636	86.84	86.87
68.50	0.460	75.57	75.61	80.093	176.17	81.8	0.637	86.92	86.94
69.00	0.465	76.02	76.05	80.042	176.07	81.9	0.639	87.00	87.02
69.50	0.471	76.46	76.50	80.000	176.00	82.1	0.642	87.16	87.18
70.00	0.477	76.91	76.94	79.952	175.91	82.2	0.644	87.24	87.27
70.50	0.483	77.35	77.39	79.906	175.83	82.4	0.647	87.40	87.42
71.00	0.489	77.79	77.82	79.862	175.75	82.6	0.650	87.56	87.58
71.50	0.495	78.23	78.27	79.813	175.66	82.7	0.652	87.64	87.67

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
72.00	0.502	78.67	78.71	79.767	175.58	82.9	0.655	87.80	87.82
72.50	0.508	79.11	79.14	79.721	175.50	83.1	0.658	87.96	87.98
73.00	0.514	79.54	79.57	79.683	175.43	83.3	0.661	88.12	88.14
73.50	0.520	79.98	80.01	79.630	175.33	83.4	0.663	88.20	88.22
74.00	0.527	80.41	80.44	79.585	175.25	83.6	0.666	88.36	88.38
74.50	0.533	80.84	80.87	79.541	175.17	83.8	0.669	88.52	88.54
75.00	0.540	81.27	81.30	79.505	175.11	84.0	0.672	88.68	88.70
75.50	0.547	81.70	81.72	79.452	175.01	84.1	0.674	88.76	88.78
76.00	0.553	82.12	82.15	79.404	174.93	84.3	0.678	88.92	88.93
76.50	0.560	82.54	82.57	79.362	174.85	84.5	0.681	89.07	89.09
77.00	0.567	82.97	82.99	79.316	174.77	84.7	0.684	89.23	89.25
77.50	0.574	83.39	83.42	79.271	174.69	84.9	0.687	89.39	89.40
78.00	0.581	83.80	83.83	79.227	174.60	85.1	0.691	89.54	89.56
78.50	0.588	84.22	84.25	79.183	174.53	85.2	0.693	89.62	89.64
79.00	0.595	84.64	84.66	79.133	174.44	85.4	0.696	89.78	89.79
79.50	0.603	85.05	85.07	79.094	174.37	85.6	0.699	89.93	89.95
80.00	0.610	85.46	85.48	79.050	174.29	85.8	0.703	90.09	90.10
80.50	0.618	85.87	85.89	79.008	174.21	86.1	0.708	90.32	90.33
81.00	0.625	86.27	86.30	78.968	174.14	86.3	0.711	90.47	90.48
81.50	0.633	86.68	86.70	78.925	174.07	86.5	0.715	90.62	90.64
82.00	0.641	87.08	87.11	78.879	173.98	86.8	0.720	90.86	90.87
82.50	0.648	87.48	87.51	78.844	173.92	87.0	0.724	91.01	91.02
83.00	0.656	87.88	87.91	78.806	173.85	87.2	0.728	91.16	91.17
83.50	0.664	88.28	88.30	78.767	173.78	87.5	0.733	91.39	91.40

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TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
84.00	0.673	88.68	88.70	78.723	173.70	87.7	0.737	91.54	91.56
84.50	0.681	89.07	89.09	78.668	173.64	88.0	0.741	91.77	91.78
85.00	0.689	89.46	89.48	78.645	173.56	88.2	0.746	91.92	91.93
85.50	0.698	89.85	89.87	78.613	173.50	88.5	0.751	92.14	92.16
86.00	0.706	90.24	90.26	78.575	173.44	88.8	0.756	92.37	92.38
86.50	0.715	90.62	90.64	78.543	173.38	89.1	0.762	92.59	92.60
87.00	0.724	91.01	91.02	78.530	173.35	89.4	0.767	92.81	92.82
87.50	0.733	91.39	91.40	78.475	173.26	89.7	0.773	93.04	93.04
88.00	0.741	91.77	91.78	78.445	173.20	90.0	0.779	93.25	93.27
88.50	0.751	92.14	92.16	78.411	173.14	90.3	0.784	93.47	93.48
89.00	0.760	92.52	92.53	78.385	173.09	90.6	0.790	93.69	93.70
89.50	0.769	92.89	92.90	78.350	173.03	90.9	0.796	93.91	93.92
90.00	0.779	93.25	93.26	78.323	172.98	91.2	0.802	94.13	94.13
90.50	0.788	93.62	93.63	78.295	172.93	91.6	0.809	94.41	94.42
91.00	0.798	93.98	93.99	78.270	172.89	91.9	0.816	94.63	94.63
91.50	0.808	94.34	94.35	78.265	172.88	92.3	0.824	94.91	94.92
92.00	0.818	94.70	94.71	78.259	172.87	92.6	0.831	95.13	95.13
92.50	0.828	95.05	95.06	78.241	172.83	93.0	0.839	95.41	95.42
93.00	0.839	95.41	95.41	78.227	172.81	93.4	0.847	95.69	95.69
93.50	0.849	95.76	95.76	78.211	172.78	93.8	0.855	95.97	95.97
94.00	0.860	96.10	96.11	78.195	172.75	94.2	0.864	96.24	96.24
94.50	0.871	96.45	96.45	78.186	172.73	94.7	0.874	96.58	96.58
95.00	0.881	96.79	96.79	78.177	172.72	95.1	0.883	96.86	96.86
95.50	0.892	97.125	97.129	78.174	172.713	95.55	0.893	97.158	97.164

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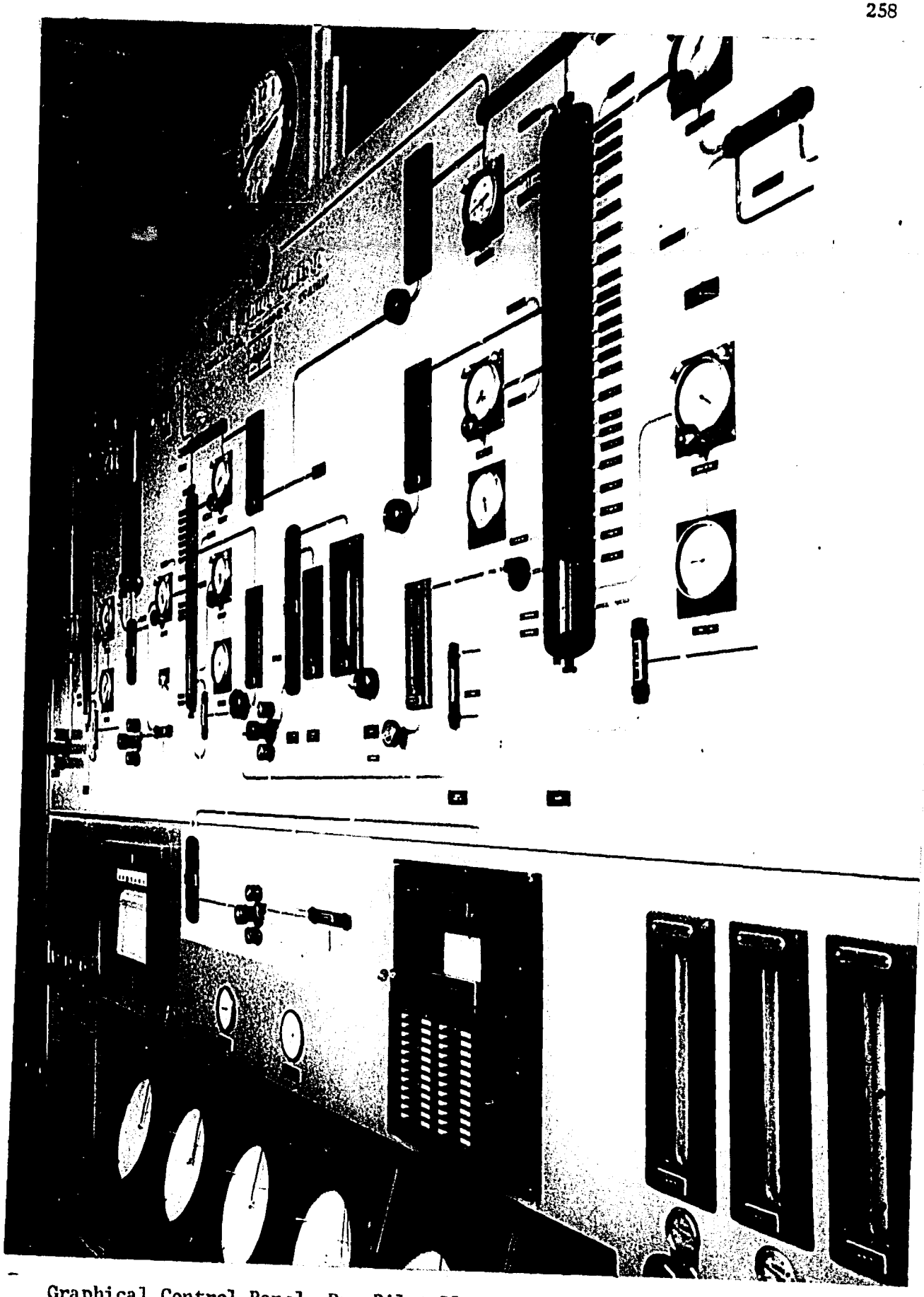
TABLE LXI (Continued)

EQUILIBRIUM COMPOSITIONS FOR THE SYSTEM ETHANOL-WATER AT ONE ATMOSPHERE

Ethanol in the Liquid Phase				Boiling Temperature		Ethanol in the Vapor Phase			
Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C	°C	°F	Weight %	Mole Fraction	% Volume 60°F	% Volume 20°C
95.58	0.8943	97.179	97.184	78.174	172.713	95.58	0.8943	97.179	97.184
96.00	0.903	97.459	97.464	78.174	172.713	95.88	0.901	97.379	97.381
96.50	0.915	97.79	97.79	78.179	172.72	96.3	0.911	97.66	97.66
97.00	0.927	98.12	98.12	78.181	172.73	96.8	0.923	97.99	97.98
97.50	0.938	98.44	98.44	78.191	172.74	97.3	0.934	98.31	98.32
98.00	0.950	98.76	98.76	78.205	172.77	97.8	0.946	98.63	98.63
98.50	0.963	99.08	99.07	78.222	172.80	98.4	0.960	99.01	99.01
99.00	0.975	99.39	99.39	78.243	172.84	98.9	0.972	99.32	99.32
99.50	0.987	99.70	99.70	78.270	172.89	99.4	0.985	99.63	99.63
100.00	1.000	100.00	100.00	78.300	172.94	100.00	1.000	100.00	100.00



Graphical Control Panel, Rum Pilot Plant, Agricultural Experiment Station, University of Puerto Rico.

AUTOBIOGRAPHY

Herminio M. Brau was born in Cabo Rojo, Puerto Rico, on August 27, 1922. He attended the Cabo Rojo public schools graduating from the Pedro F. Colberg Grammar School in 1936 and from the Cabo Rojo High School in 1940. He entered the College of Agriculture and Mechanical Arts of the University of Puerto Rico, at Mayaguez, Puerto Rico, in the fall of 1940, where he was awarded the degree of Bachelor of Science in Chemical Engineering in May 1944. Immediately upon graduation, he entered into active duty in the United States Armed Forces attending the Officers Candidate School, at Fort Benning, Georgia, where he received his commission as a Second Lieutenant in October, 1944. Since his discharge from the service, in July 1946 to the present, he has been a member of the Technical Staff of the Agricultural Experiment Station of the University of Puerto Rico. In the fall of 1948, he entered New York University, at New York City, where he received the degree of Master of Chemical Engineering in May 1949. He attended the Graduate School of Louisiana State University during the academic years of 1951-52 and 1955-56 and is at present a candidate for the Doctor of Philosophy Degree.

EXAMINATION AND THESIS REPORT

Candidate: Herminio M. Brau

Major Field: Chemical Engineering

Title of Thesis: Higher Alcohols in the Alcoholic Distillation from Fermented Cane Molasses

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 10, 1956